Effects of Grafting Density on Block Polymer Self-Assembly: From Linear to Bottlebrush

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SUPPORTING INFORMATION

Table S1. Total molecular weights (M_n), total backbone degrees of polymerization (N_{bb}), and lamellar periods (d^*) for (PLA^x-*r*-DME^{1-x})$_n$-*b*-(PS^x-*r*-DBE^{1-x})$_n$ graft block polymers (System I).

z	Sample ID	M_n (kDa)	N_{bb}	d^* (nm)
1.00	**A1**	158	44	27.5
	A2	304	84	46.0
	A3	465	129	65.8
	A4	596	165	82.0
	A5	718	199	97.5
0.75	**B1**	234	84	40.3
	B2	361	130	58.2
	B3	467	168	72.5
	B4	606	219	89.5
0.50	**C1**	166	86	35.0
	C2	243	126	47.6
	C3	315	163	58.7
	C4	400	207	71.5
0.35	**D1**	124	87	29.7
	D2	181	127	40.5
	D3	238	167	50.5
	D4	301	211	62.0
	D5	369	258	71.5
	D6	430	301	81.0
0.25	**E1**	98.8	90	27.9
	E2	146	134	36.7
	E3	167	153	41.5
	E4	200	183	47.0
	E5	216	197	51.5
	E6	244	223	55.5
	E7	286	262	63.5
0.20	**F1**	119	128	33.6
	F2	153	166	42.5
	F3	195	211	50.0
	F4	216	234	55.0
	F5	230	249	57.5
	F6	248	268	61.0
	F7	294	318	69.0
0.15	**G1**	163	216	43.6
	G2	178	235	46.6
	G3	189	250	50.3
	G4	216	286	54.0
	G5	232	307	57.0
	G6	246	325	60.0
0.05	**H1**	91.7	218	33.5
	H2	103	246	37.0
	H3	111	264	39.0
	H4	124	294	41.2
	H5	129	308	43.0
	H6	142	339	46.2
0.00	**I1**	46.5	184	26.3
	I2	55.4	219	29.5
	I3	62.7	249	32.1
	I4	72.4	287	35.4
	I5	82.3	326	38.9
	I6	91.5	363	41.6

Table S2. Total molecular weights (M_n), total backbone degrees of polymerization (N_{bb}), and lamellar periods (d^*) for (PLA^z-*r*-DBE^{1-z})$_n$-*b*-(PS^z-*r*-DBE^{1-z})$_n$ graft block polymers (System II).

z	Sample ID	M_n (kDa)	N_{bb}	d^* (nm)
0.75	**J1**	116	44	23.5
	J2	215	82	36.8
	J3	330	125	52.4
	J4	402	152	62.6
	J5	521	198	76.0
	J6	649	246	92.0
0.50	**K1**	249	135	43.0
	K2	322	174	52.8
	K3	396	213	62.2
	K4	472	254	70.2
	K5	529	285	78.0
	K6	603	325	85.7
0.35	**L1**	241	174	46.5
	L2	307	221	55.0
	L3	364	263	62.5
	L4	436	314	71.0
	L5	472	341	78.0
	L6	538	388	85.0
0.25	**M1**	232	216	42.6
	M2	277	258	48.2
	M3	335	312	54.1
	M4	384	358	61.9
	M5	406	378	64.0
	M6	472	439	71.4
0.15	**N1**	98.5	129	24.0
	N2	161	212	32.8
	N3	193	253	37.5
	N4	213	279	41.5
	N5	251	329	46.6
	N6	299	392	51.8
0.12	**O1**	150	224	32.8
	O2	183	274	36.5
	O3	221	330	42.0
	O4	248	370	44.3
	O5	274	409	49.0
	O6	302	451	52.5
0.06	**P1**	156	324	30.3
	P2	177	367	31.8
	P3	199	413	34.2
	P4	226	469	37.3
	P5	257	533	40.4
0.05	**Q1**	152	337	27.2
	Q2	169	376	28.5
	Q3	184	408	30.0
	Q4	203	451	31.5

Table S3. Lamellar scaling laws ($d^* = b \times N_{bb}^{\alpha}$) obtained for System I using the least-square power-law fitting function in *Igor*.

z	b	α
1.00	1.033	0.858
0.75	0.999	0.835
0.50	0.926	0.815
0.35	0.838	0.801
0.25	0.788	0.788
0.20	0.781	0.779
0.15	0.778	0.751
0.05	0.750	0.707
0.00	0.737	0.685

Table S4. Lamellar scaling laws ($d^* = b \times N_{bb}^{\alpha}$) obtained for System II using the least-square power-law fitting function in *Igor*.

z	b	α
0.75	1.049	0.812
0.50	0.949	0.779
0.35	0.872	0.768
0.25	0.787	0.741
0.15	0.726	0.716
0.12	0.778	0.688
0.06	0.924	0.601
0.05	1.356	0.515

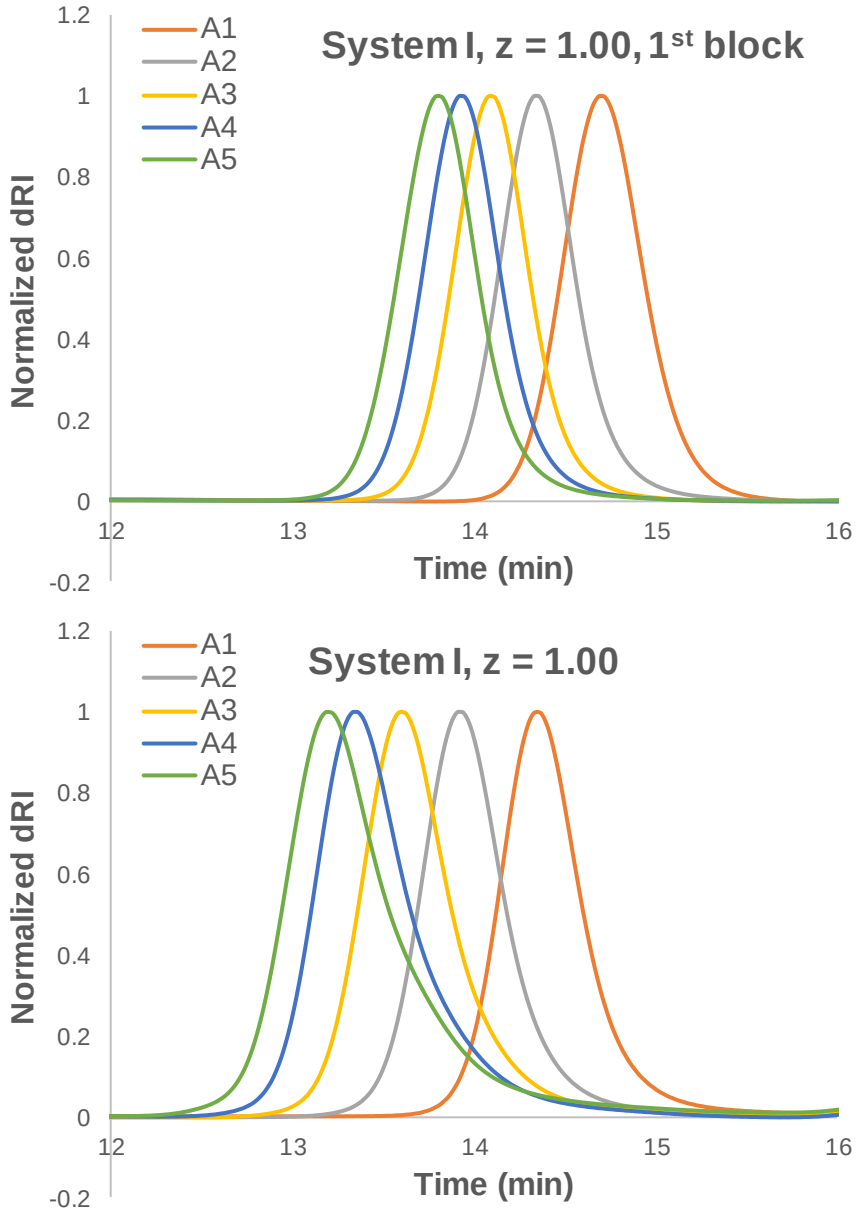


Figure S1. SEC traces.

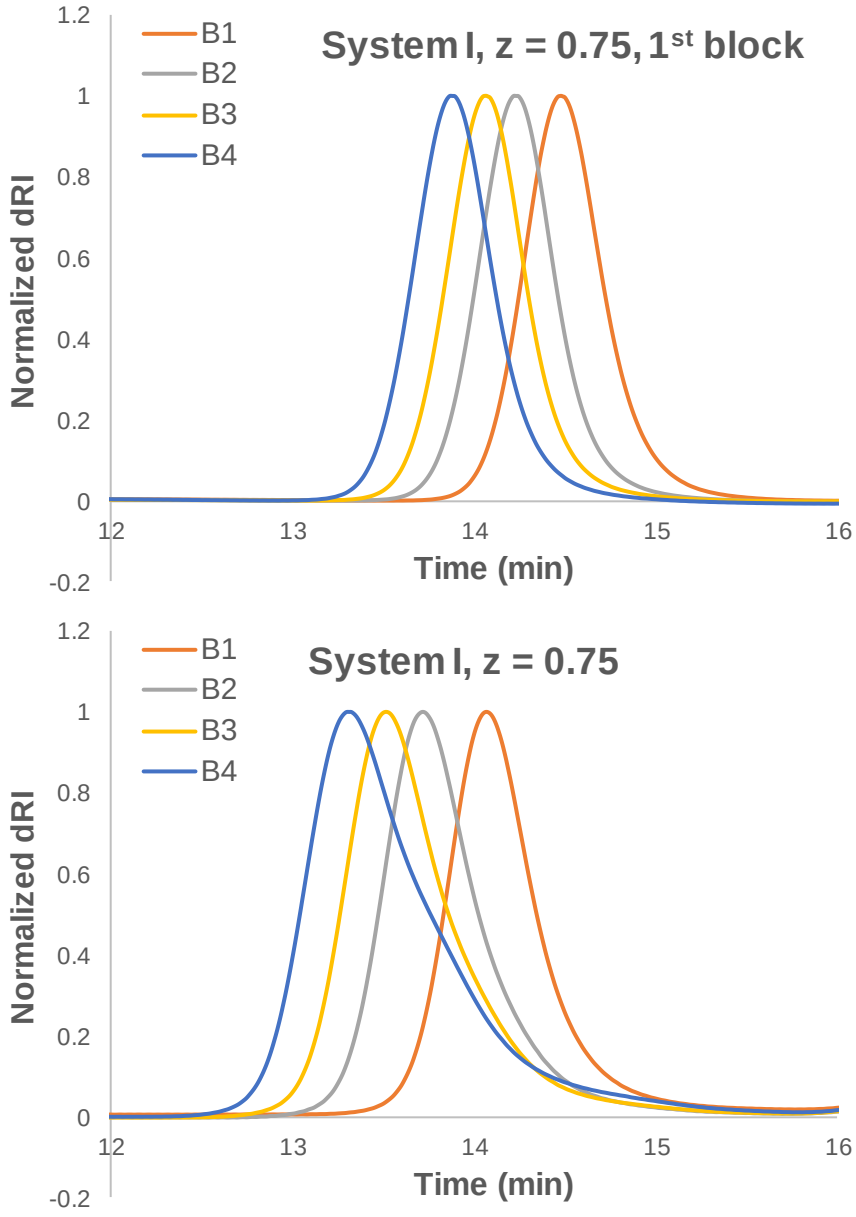
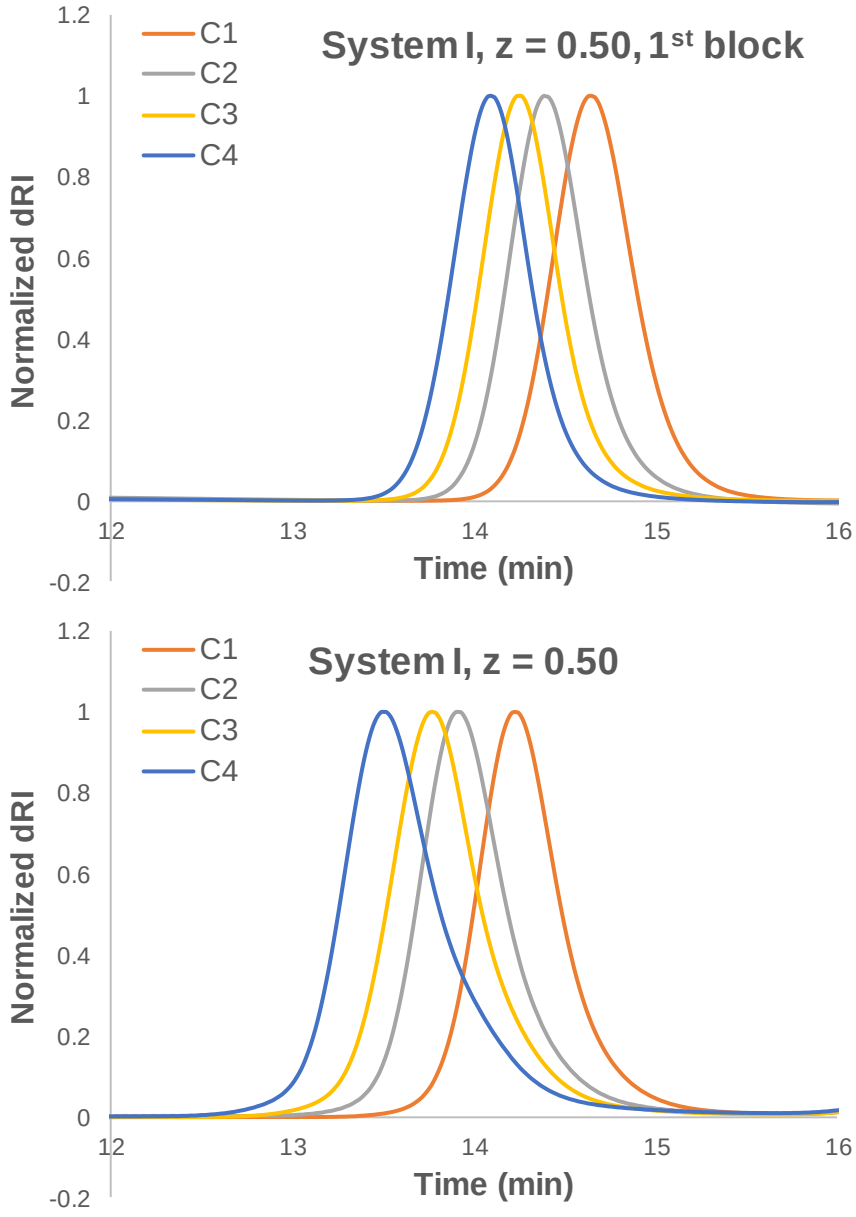


Figure S2. SEC traces.



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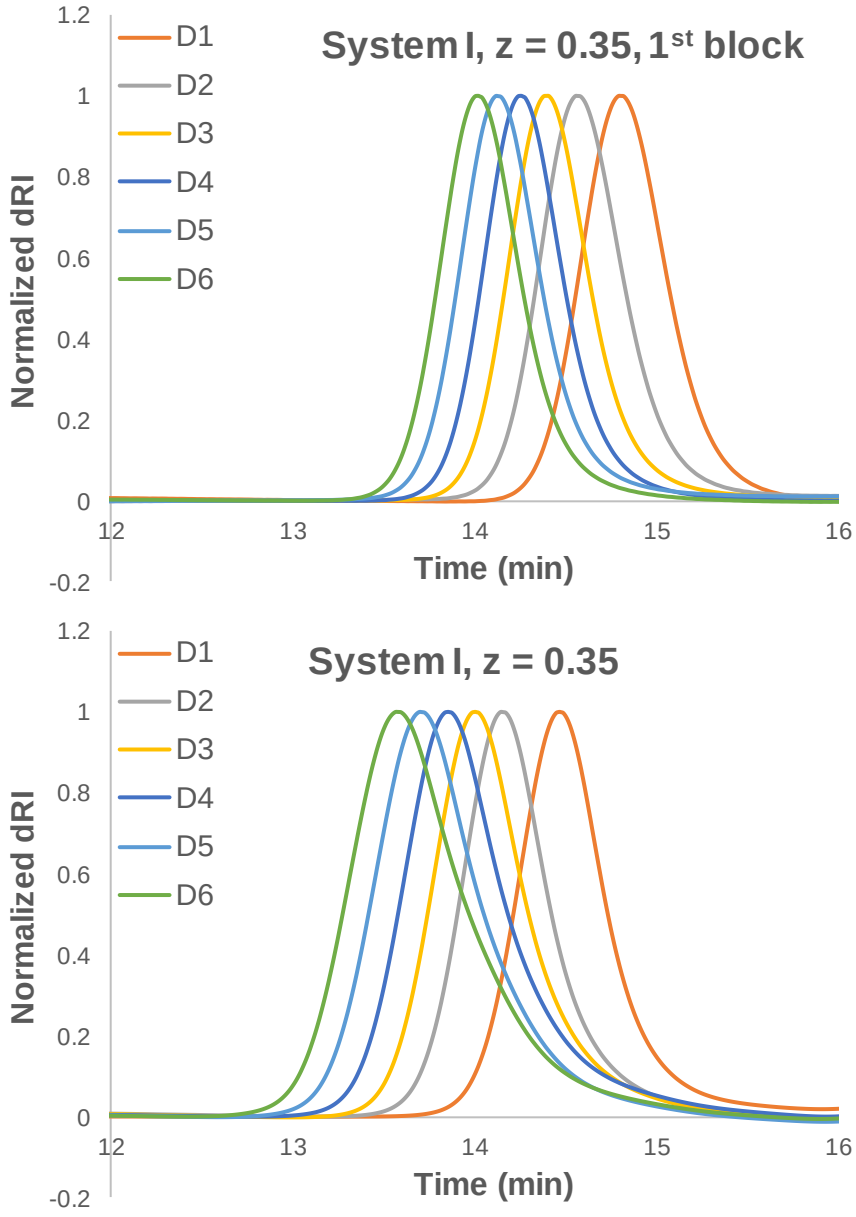

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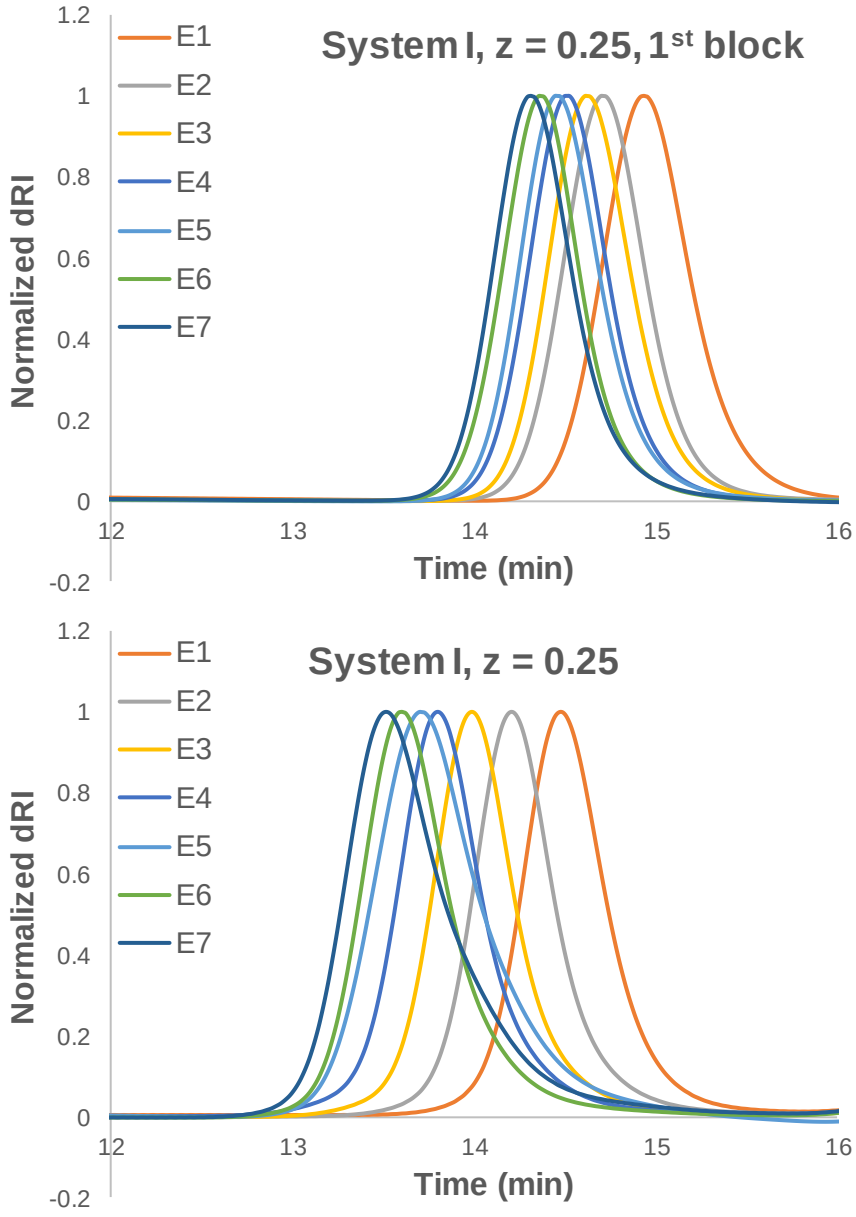

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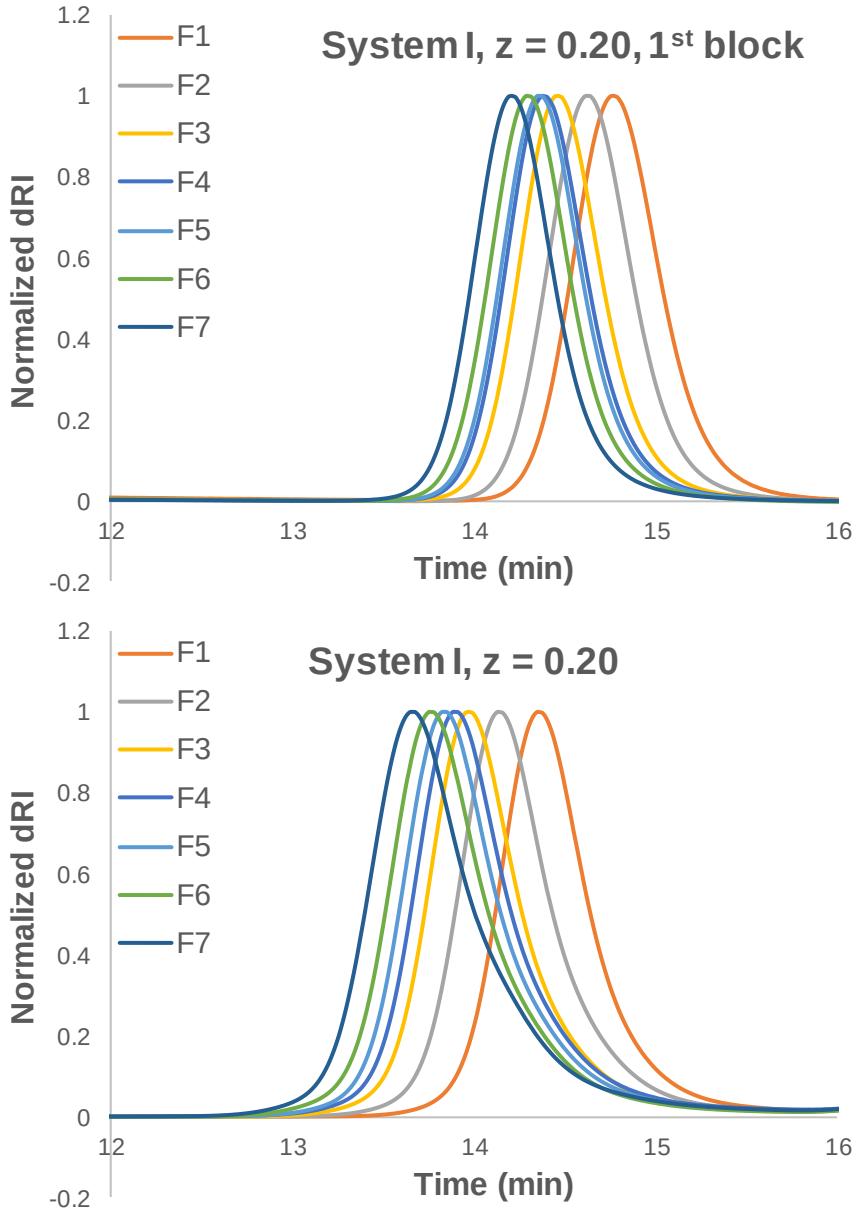

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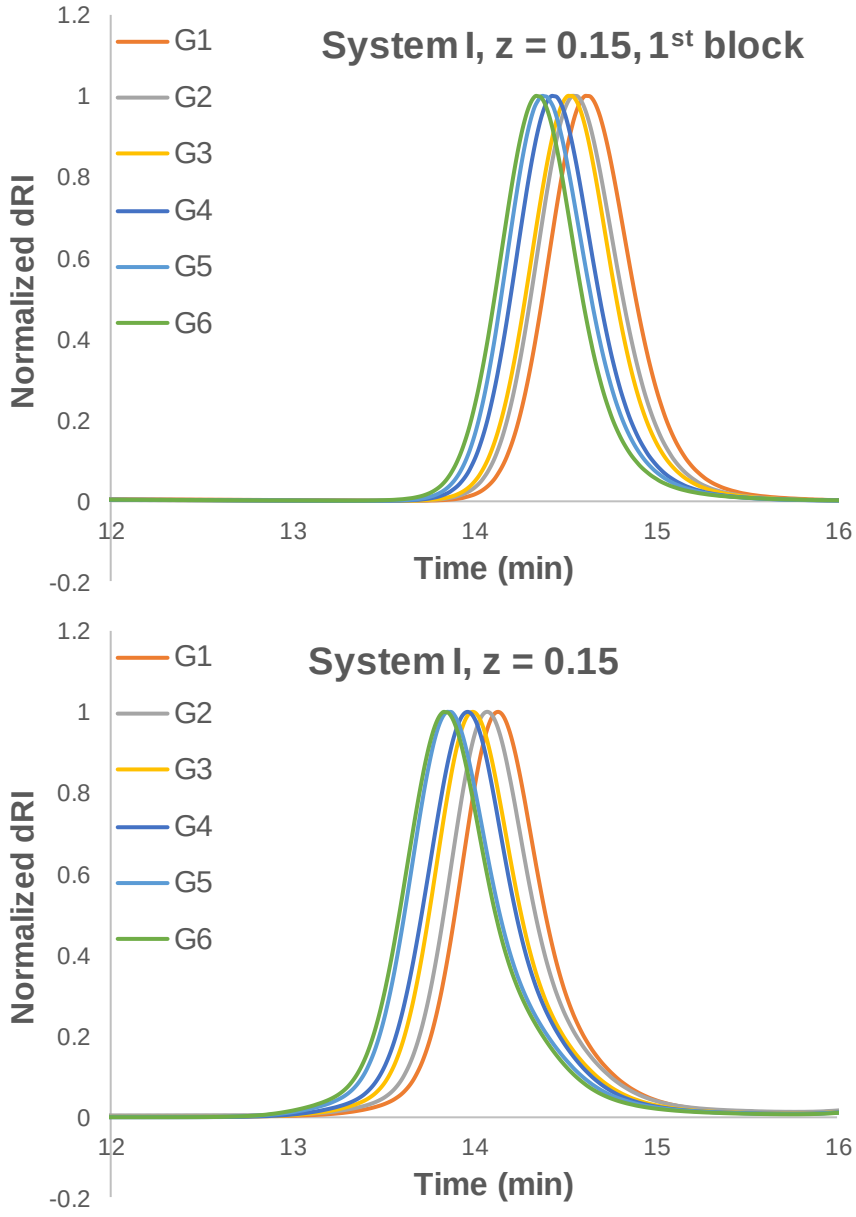

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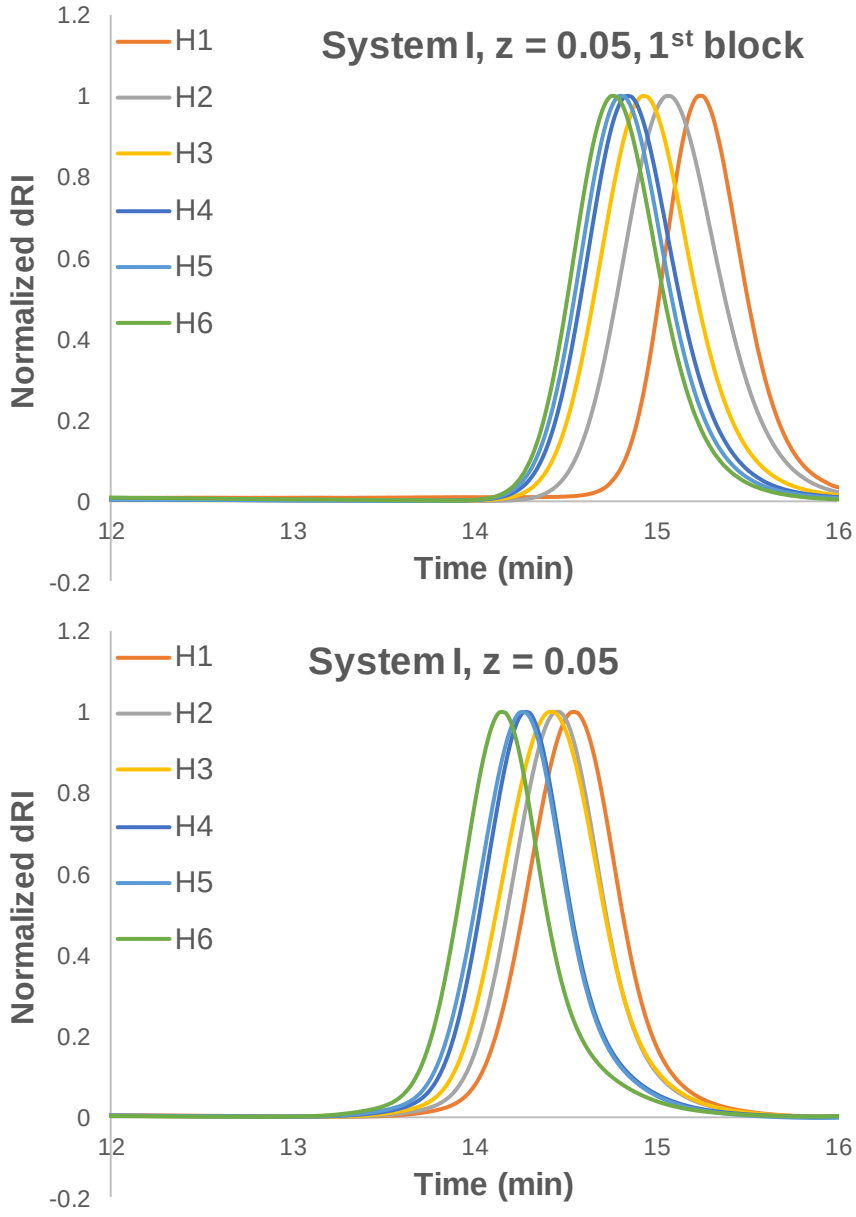

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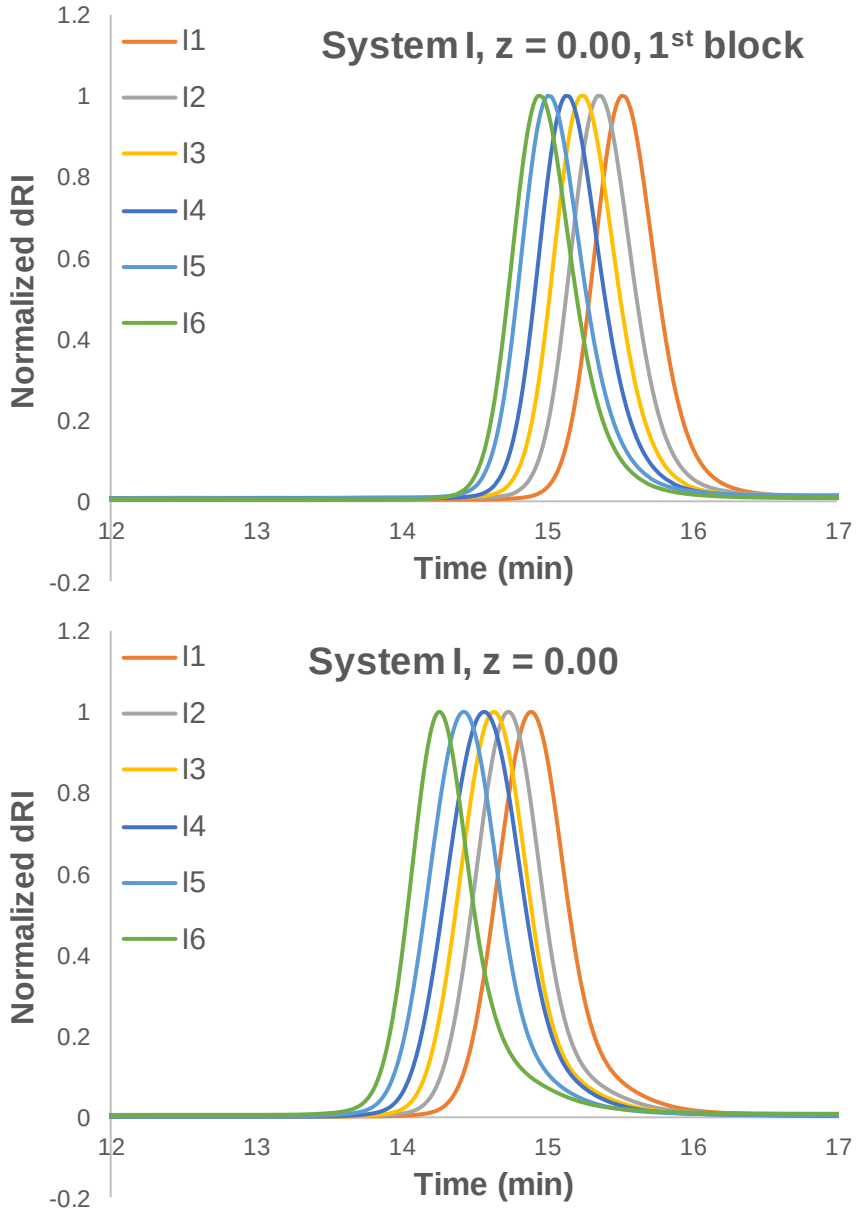

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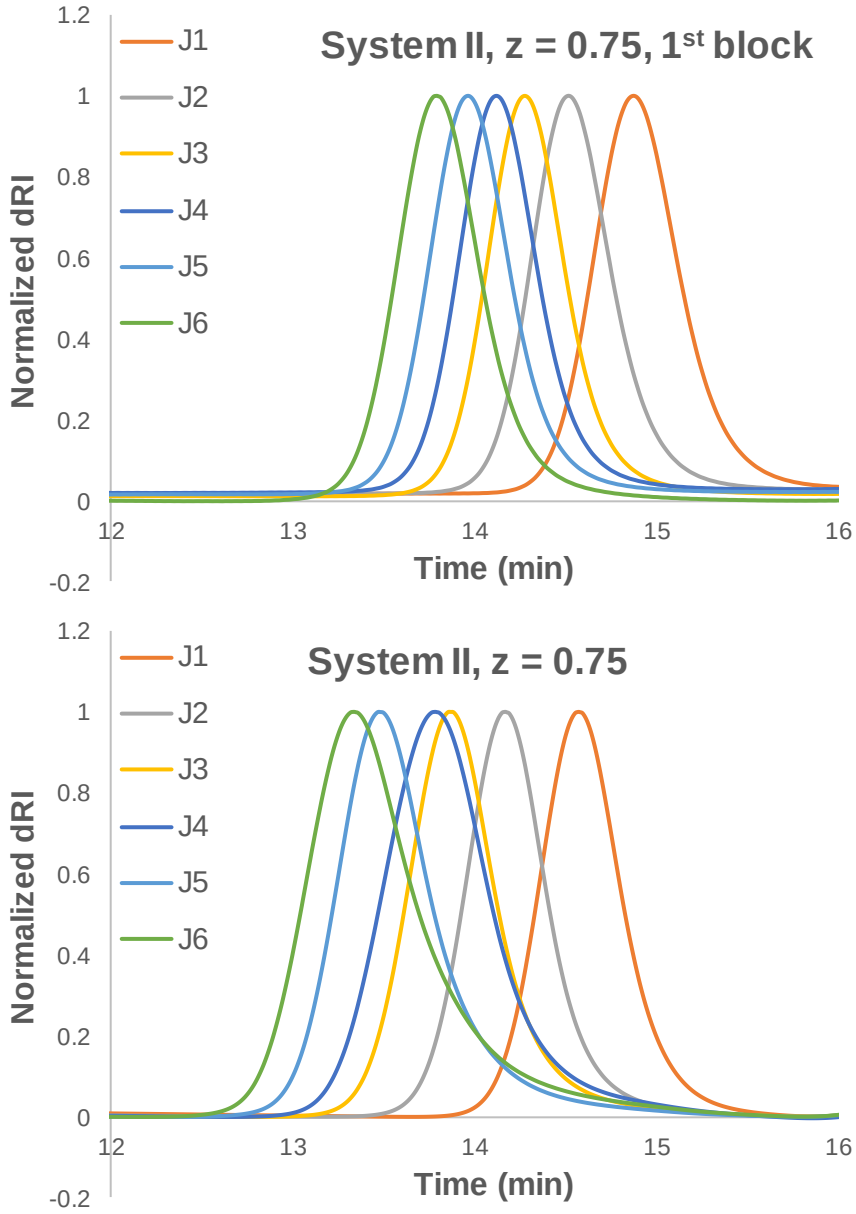

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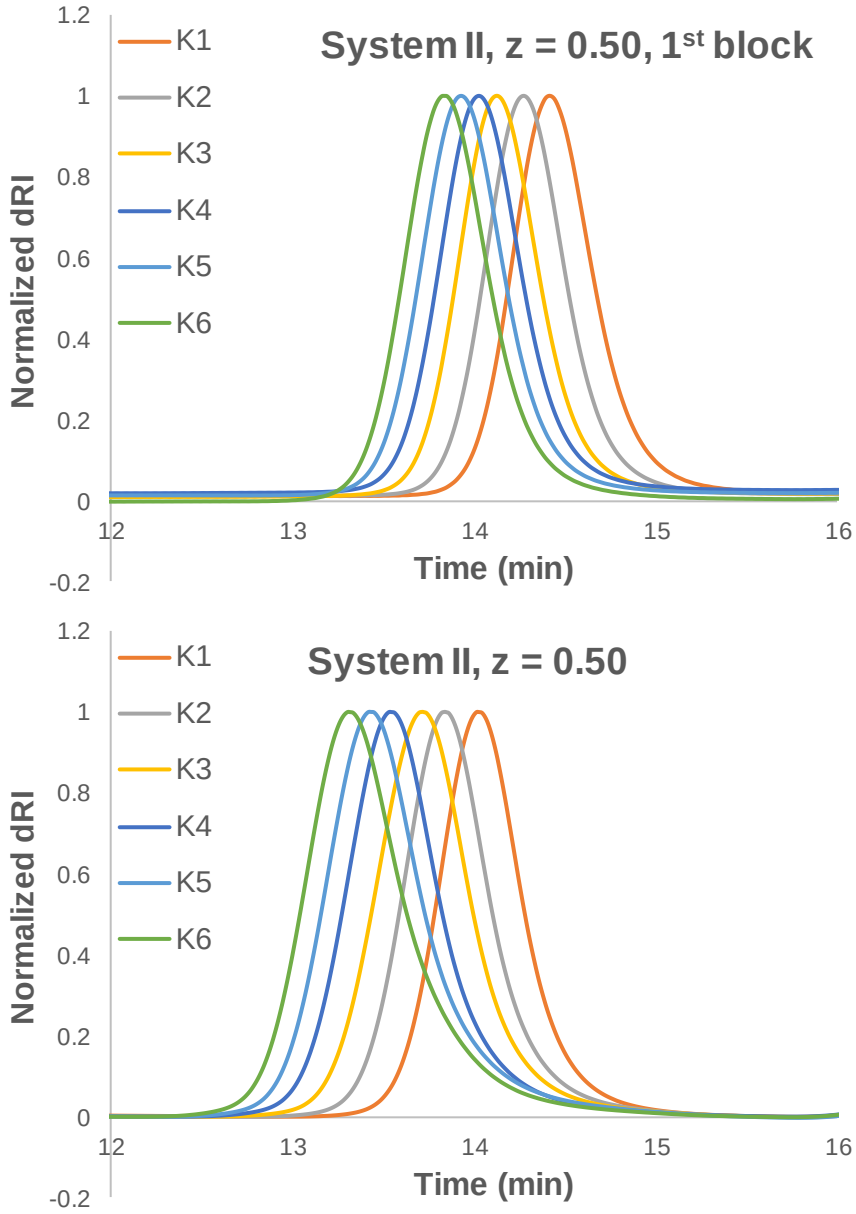

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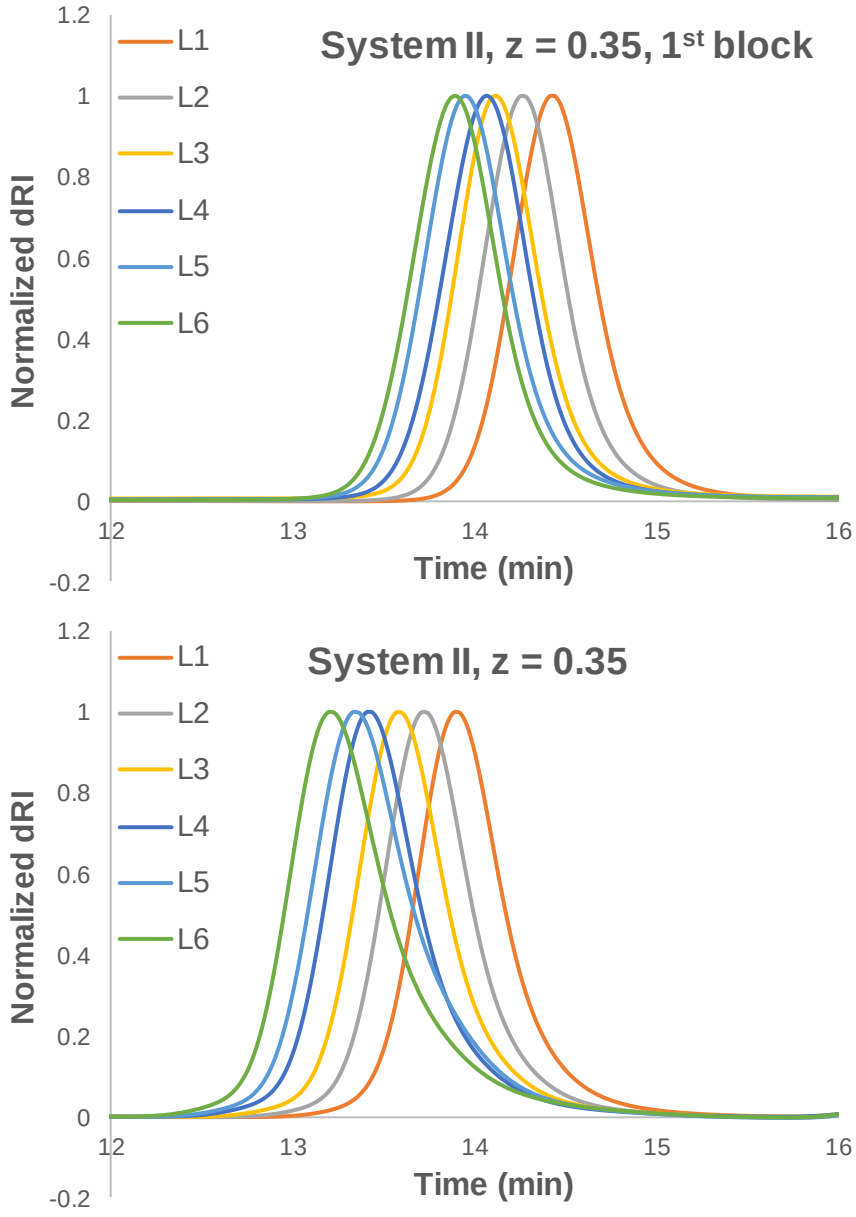

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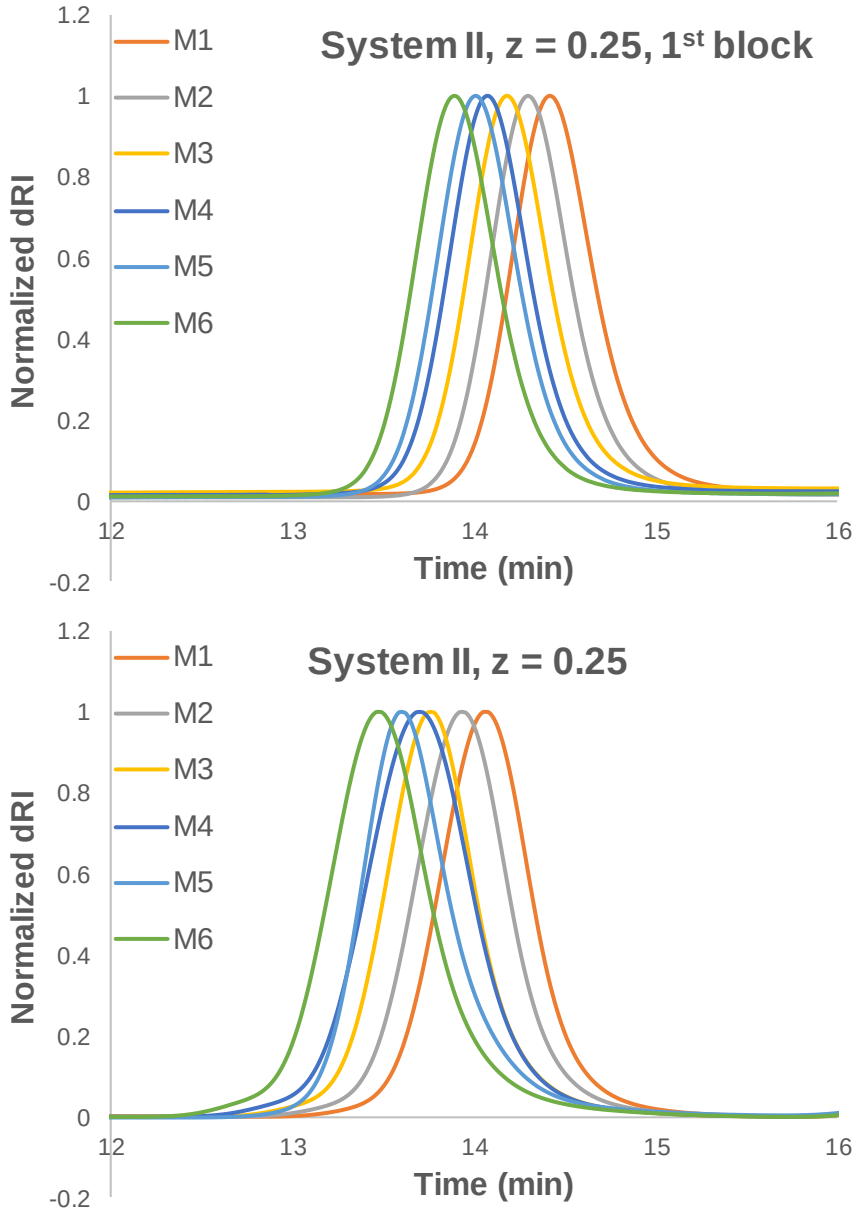

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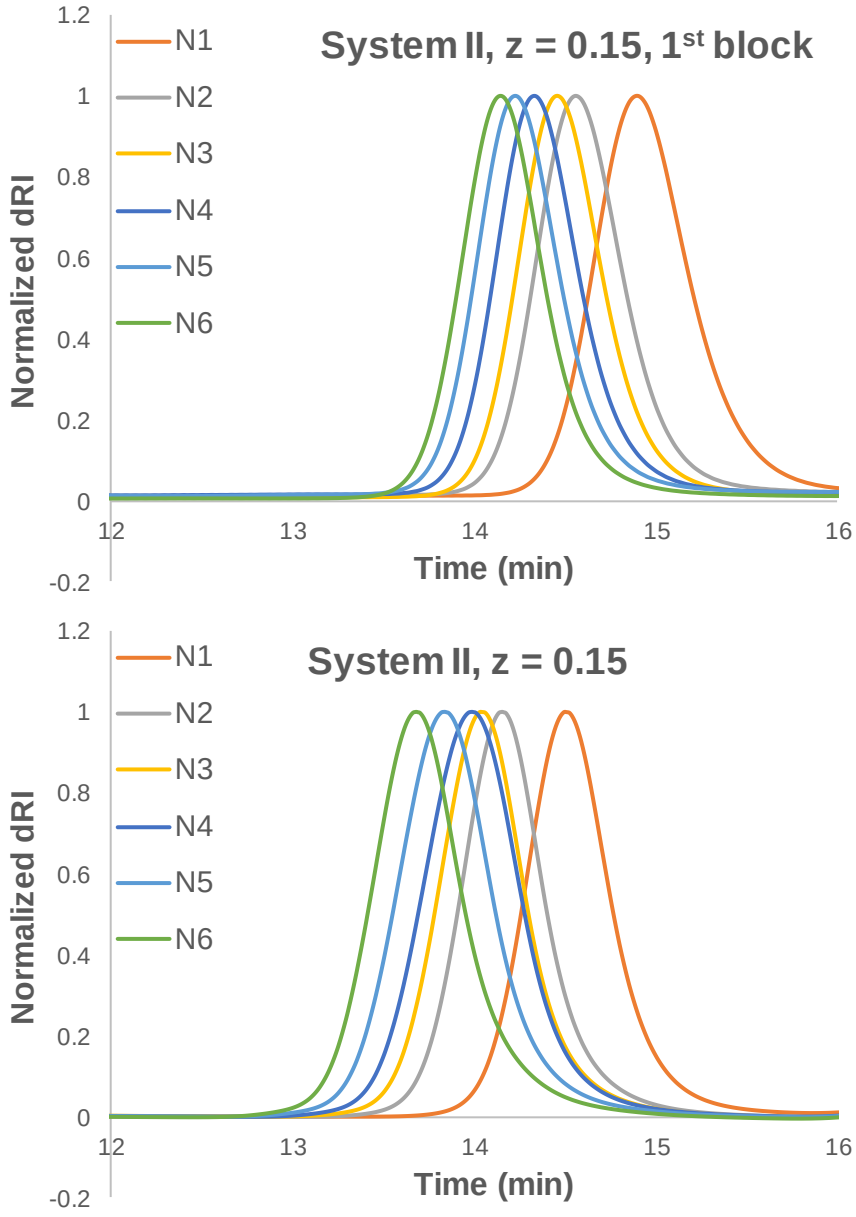

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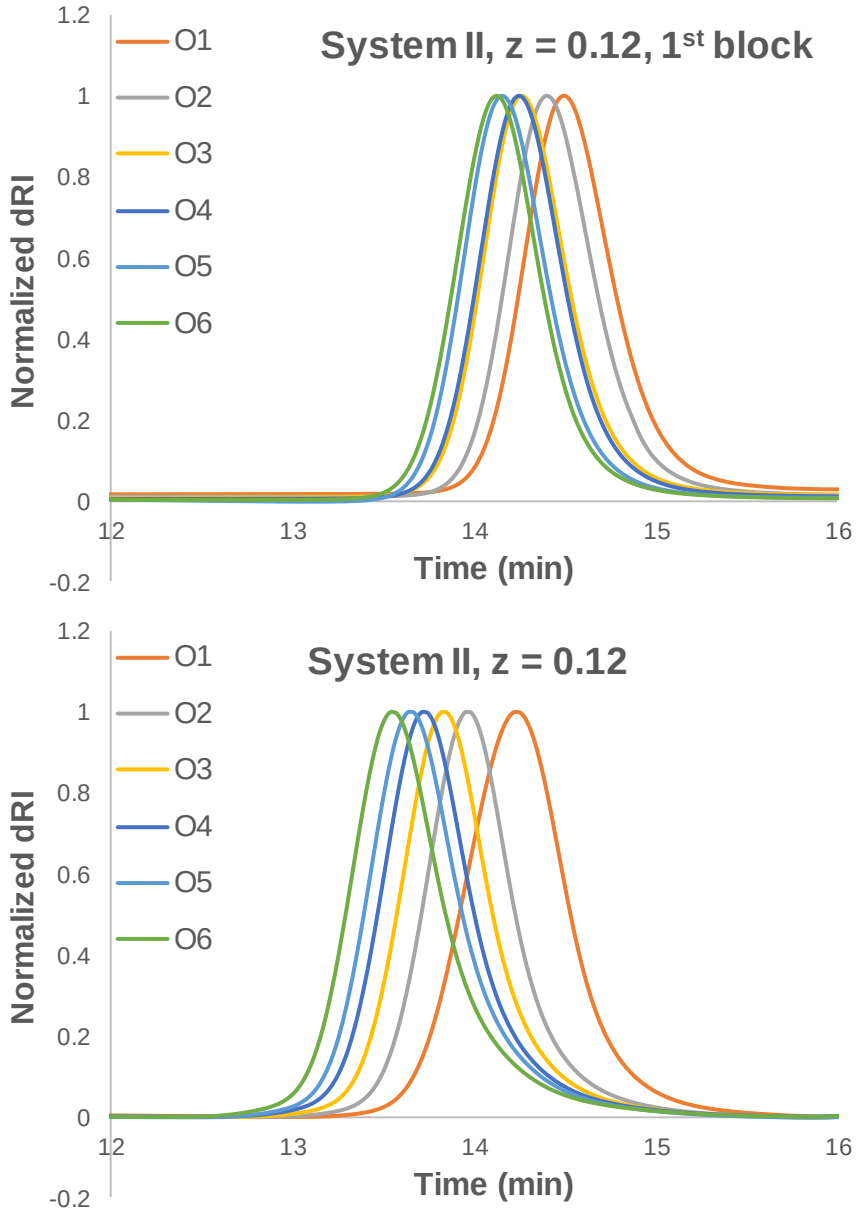

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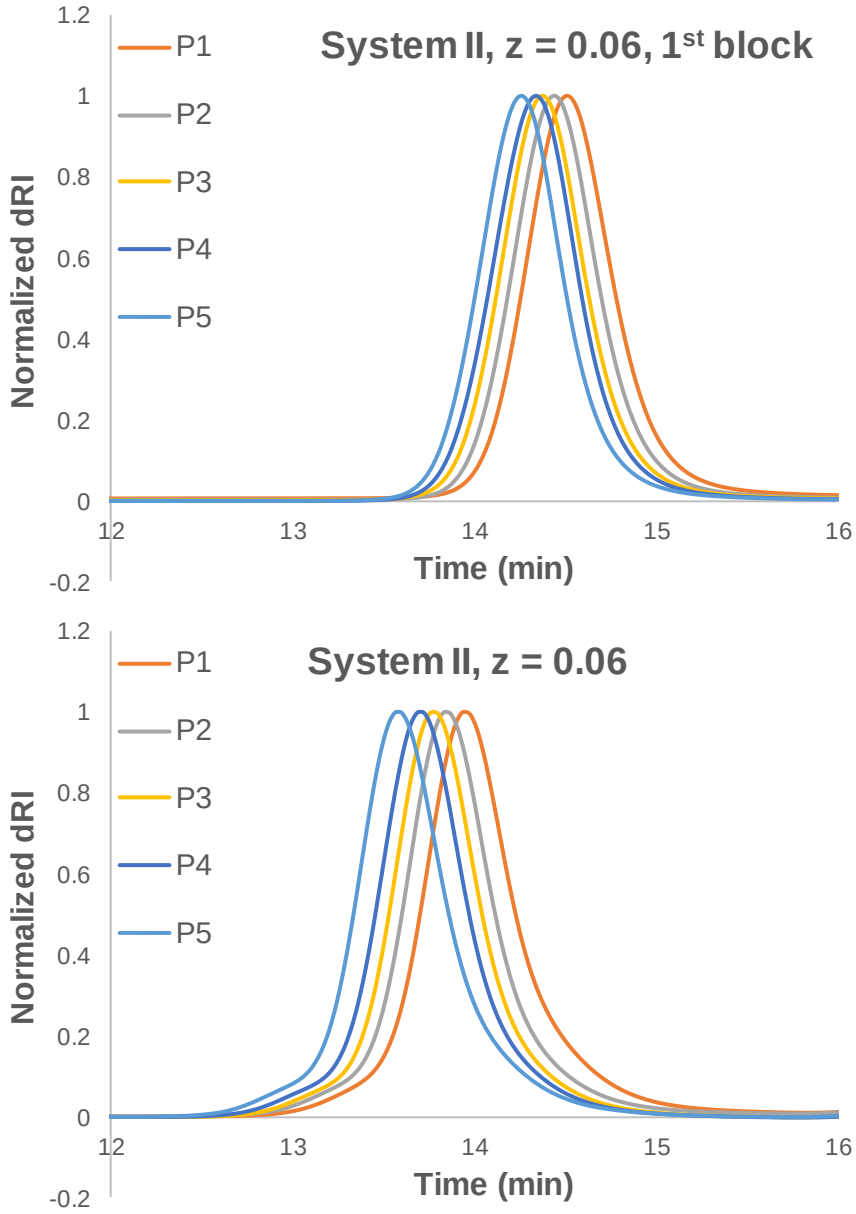
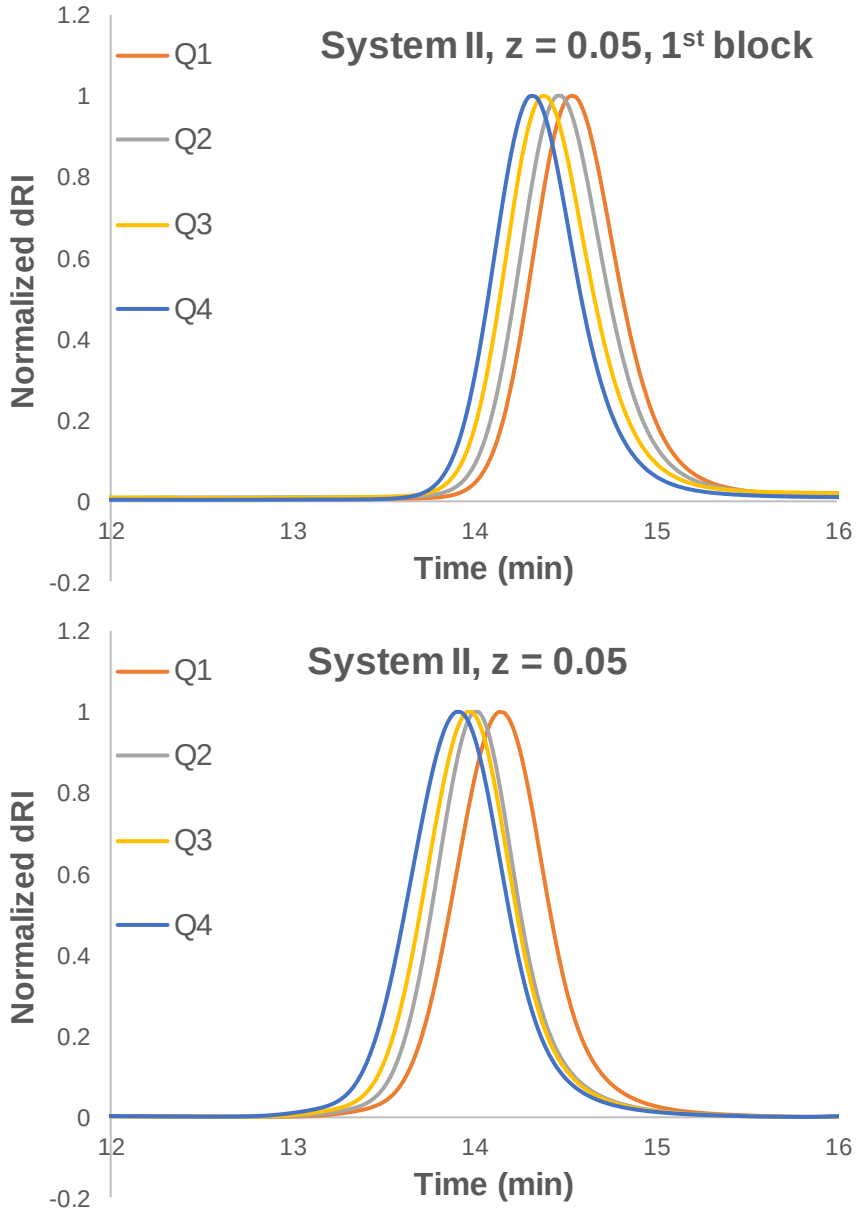


Figure S16. SEC traces.



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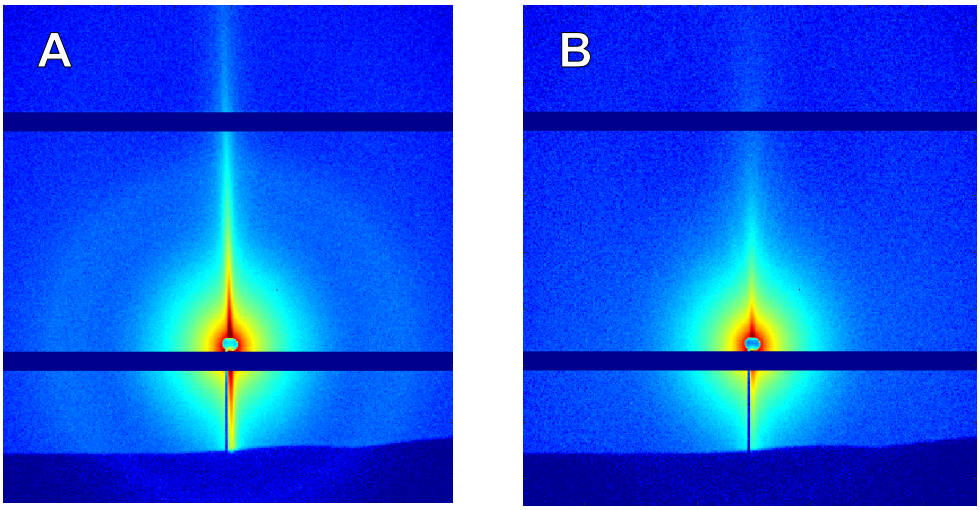
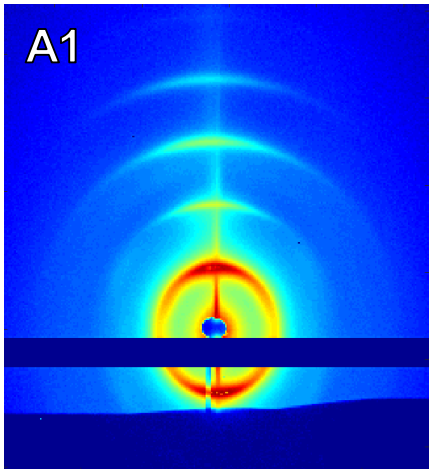


(**PLA**$^{0.05}$-*r*-**DME**$^{0.95}$)$_{200}$ (**PS**$^{0.05}$-*r*-**DBE**$^{0.95}$)$_{200}$

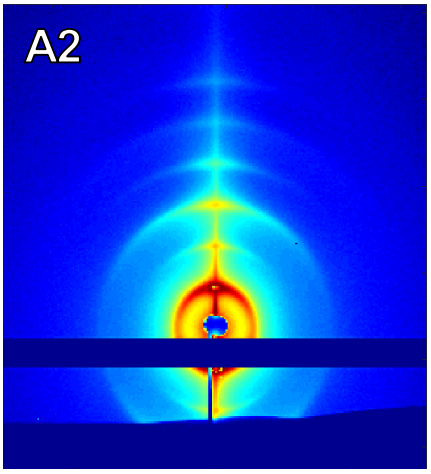
Figure S18. Raw 2D SAXS data for z = 0.05 graft polymers: (a) (**PLA**$^{0.05}$-*r*-**DME**$^{0.95}$)$_{200}$, (b) (**PS**$^{0.05}$-*r*-**DBE**$^{0.95}$)$_{200}$. These polymers correspond to each block of the lowest-grafting-density samples investigated herein. Even at large N_{bb}, no evidence of microphase separation is observed, suggesting that each block is effectively homogeneous. To a first approximation, χ between the backbone and side chains does not appear significant.

System I, z = 1.00

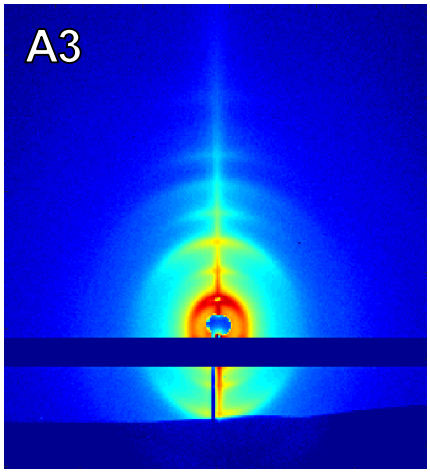
N_{bb} = 44, d^* = 27.5 nm



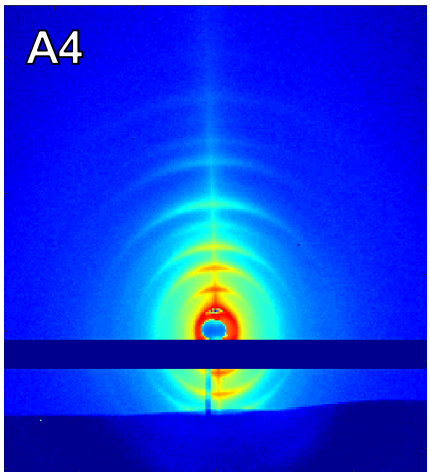
N_{bb} = 84, d^* = 46.0 nm



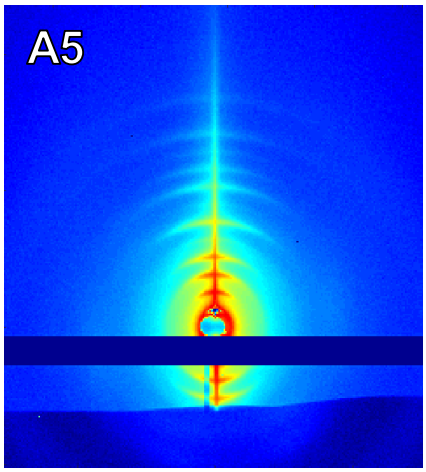
N_{bb} = 129, d^* = 65.8 nm



N_{bb} = 165, d^* = 82.0 nm

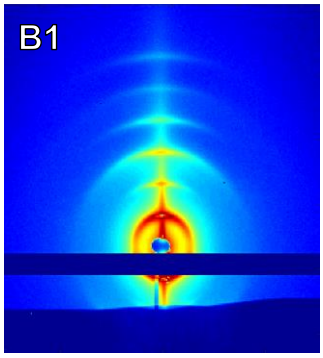


N_{bb} = 199, d^* = 97.5 nm

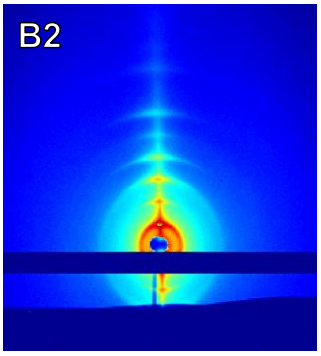


System I, *z* = 0.75

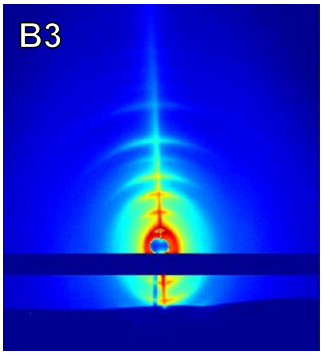
N_{bb} = 84, d^* = 40.3 nm



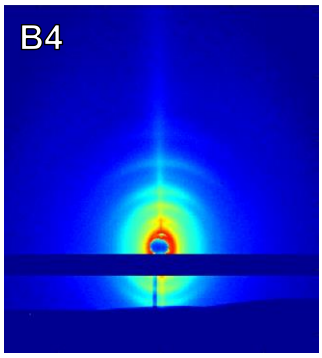
N_{bb} = 130, d^* = 58.2 nm



N_{bb} = 168, d^* = 72.5 nm

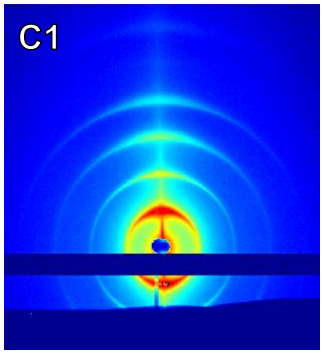


N_{bb} = 219, d^* = 89.5 nm

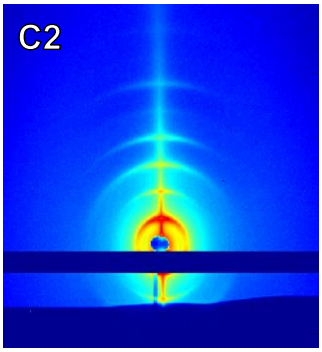


System I, *z* = 0.50

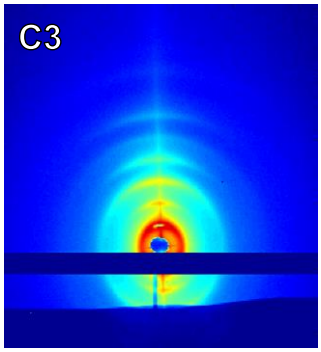
N_{bb} = 86, d^* = 35.0 nm



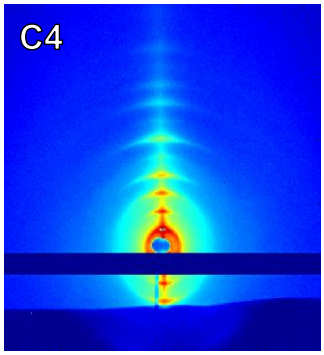
N_{bb} = 126, d^* = 47.6 nm



N_{bb} = 163, d^* = 58.7 nm

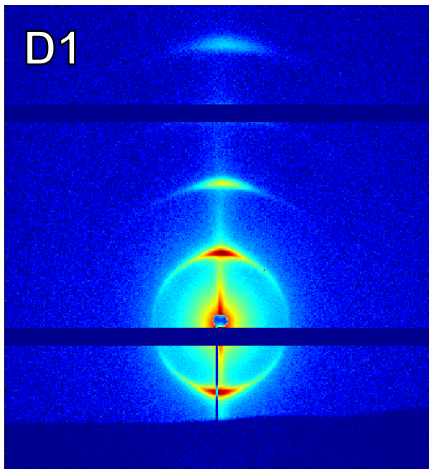


N_{bb} = 207, d^* = 71.5 nm

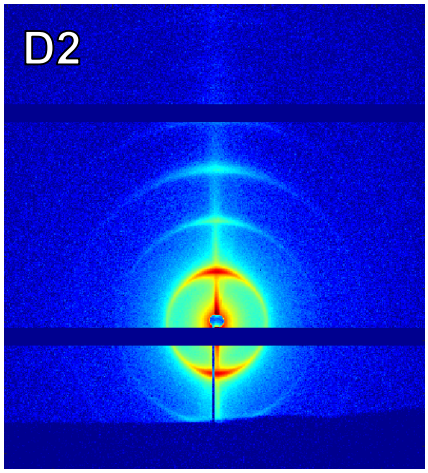


System I, z = 0.35

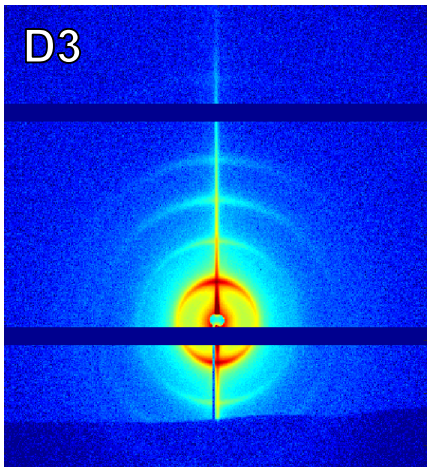
N_{bb} = 87, d^* = 29.7 nm



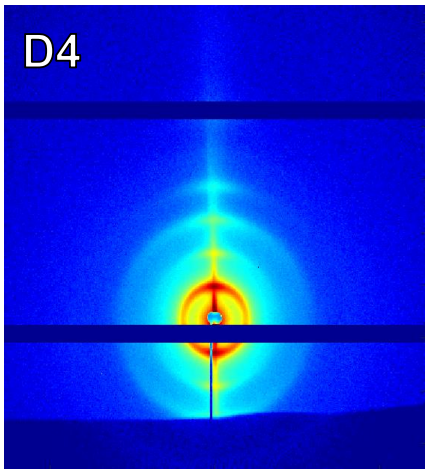
N_{bb} = 127, d^* = 40.5 nm



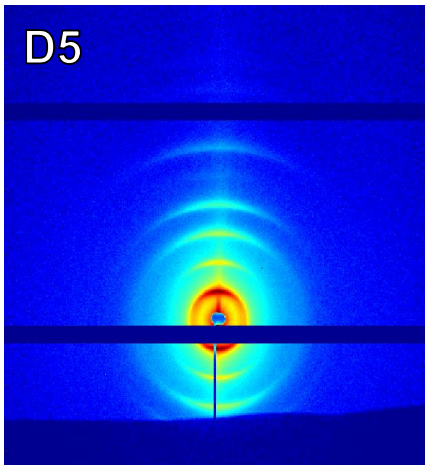
N_{bb} = 167, d^* = 50.5 nm



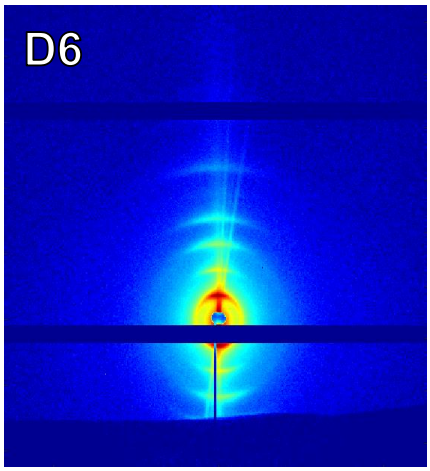
N_{bb} = 211, d^* = 62.0 nm



N_{bb} = 258, d^* = 71.5 nm

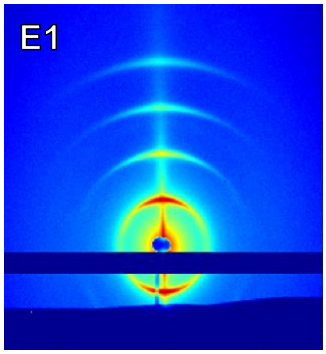


N_{bb} = 301, d^* = 81.0 nm

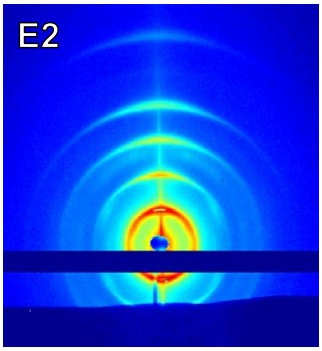


System I, z = 0.25

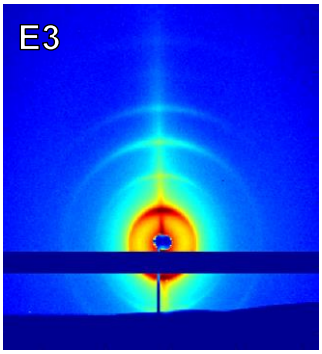
N_{bb} = 90, d^* = 27.9 nm



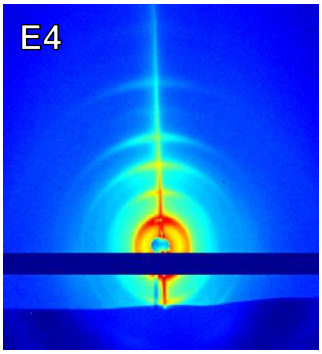
N_{bb} = 134, d^* = 36.7 nm



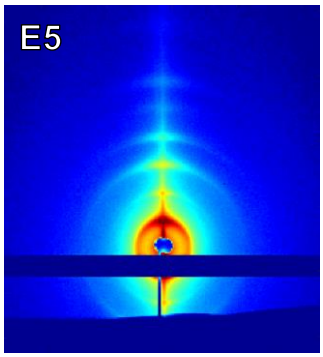
N_{bb} = 153, d^* = 41.5 nm



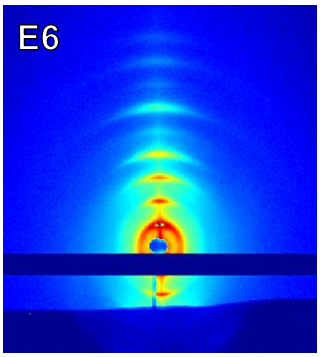
N_{bb} = 183, d^* = 47.0 nm



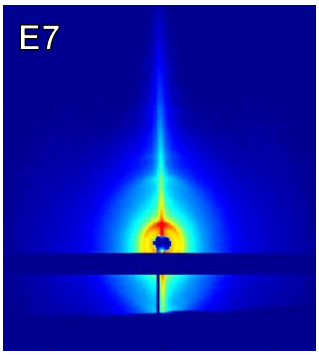
N_{bb} = 197, d^* = 51.5 nm



N_{bb} = 223, d^* = 55.5 nm



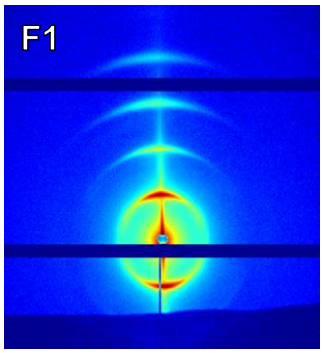
N_{bb} = 262, d^* = 63.5 nm



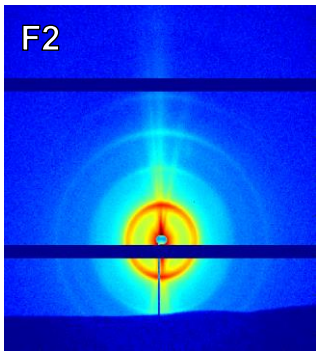
Note: **E2** exhibits minor HEX character. The intensity is weak compared to LAM. The presence of minor HEX is not expected to affect d^*.

System I, z = 0.20

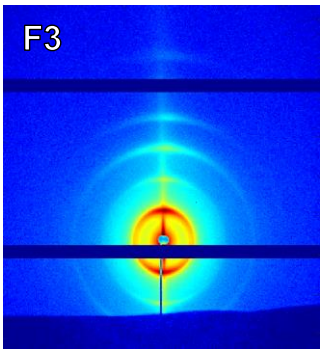
N_{bb} = 128, d^* = 33.6 nm



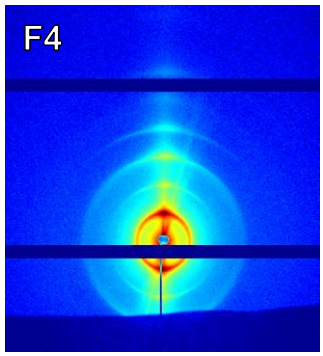
N_{bb} = 166, d^* = 42.5 nm



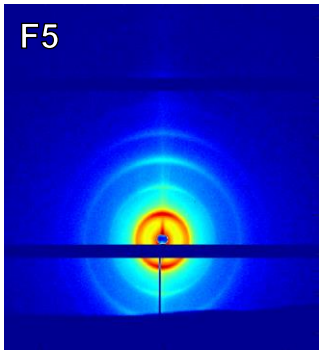
N_{bb} = 211, d^* = 50.0 nm



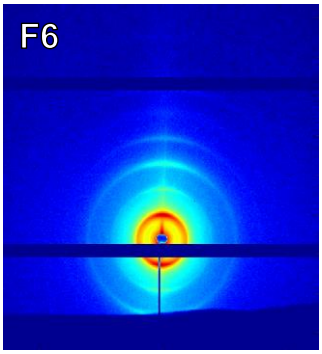
N_{bb} = 234, d^* = 55.0 nm



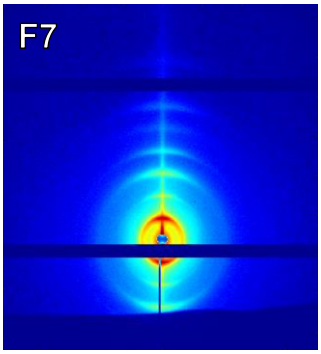
N_{bb} = 249, d^* = 57.5 nm



N_{bb} = 268, d^* = 61.0 nm

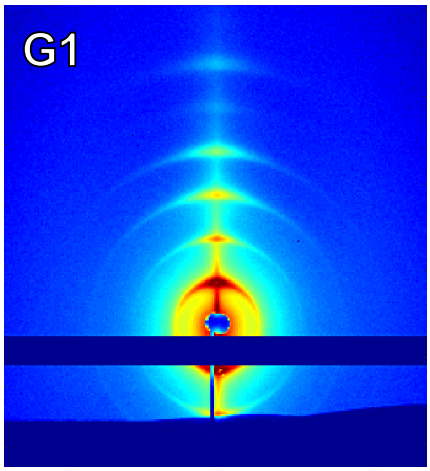


N_{bb} = 318, d^* = 69.0 nm

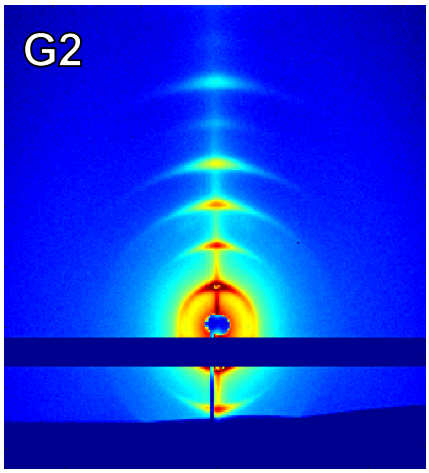


System I, z = 0.15

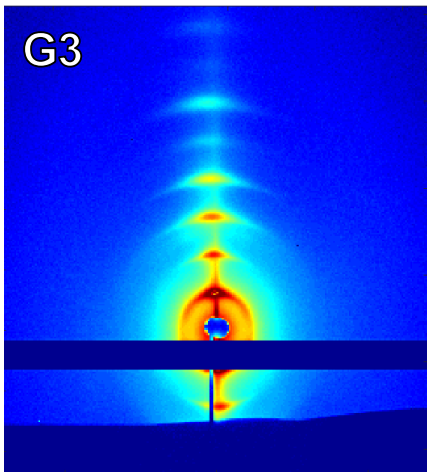
N_{bb} = 216, d^* = 43.6 nm



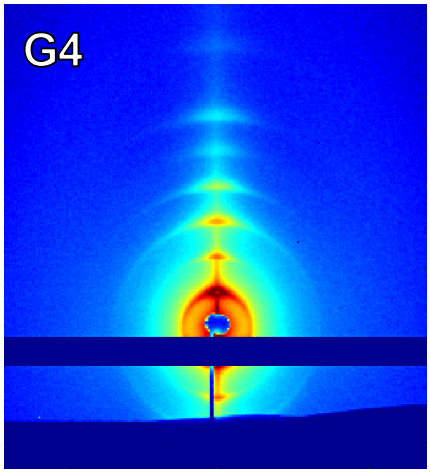
N_{bb} = 235, d^* = 46.6 nm



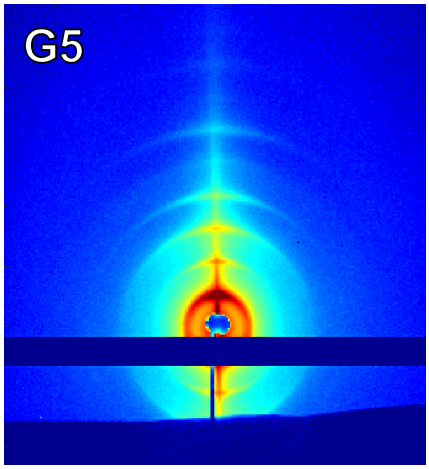
N_{bb} = 250, d^* = 50.3 nm



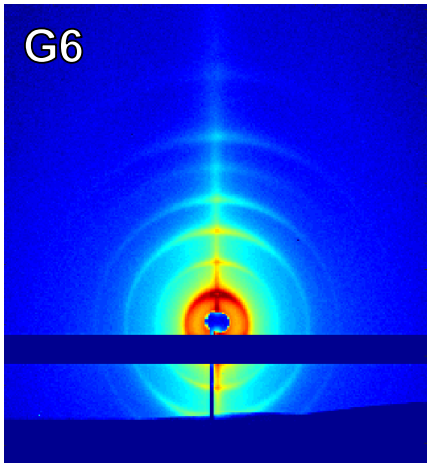
N_{bb} = 286, d^* = 54.0 nm



N_{bb} = 307, d^* = 57.0 nm

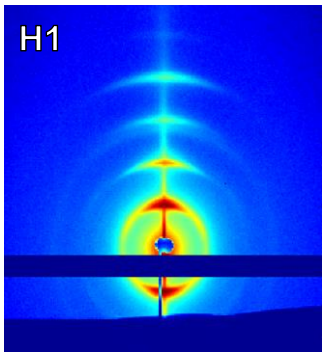


N_{bb} = 325, d^* = 60.0 nm

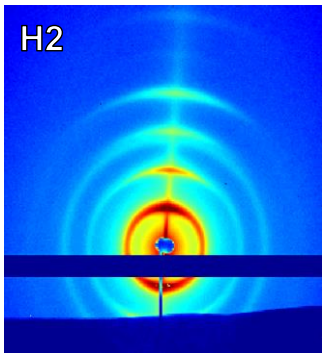


System I, z = 0.05

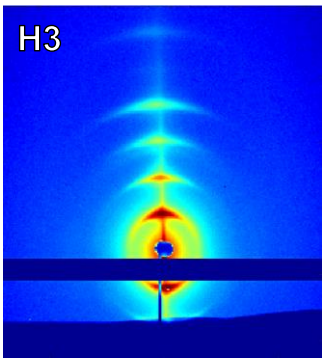
N_{bb} = 218, d^* = 33.5 nm



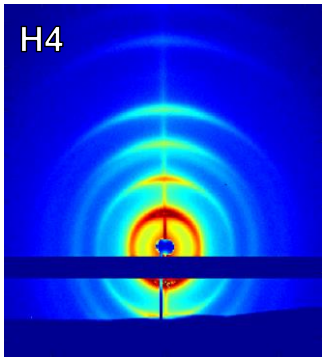
N_{bb} = 246, d^* = 37.0 nm



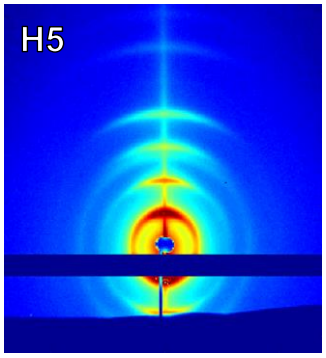
N_{bb} = 264, d^* = 39.0 nm



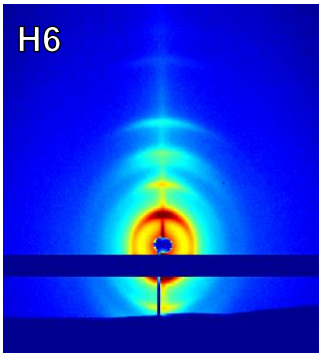
N_{bb} = 294, d^* = 41.2 nm



N_{bb} = 308, d^* = 43.0 nm



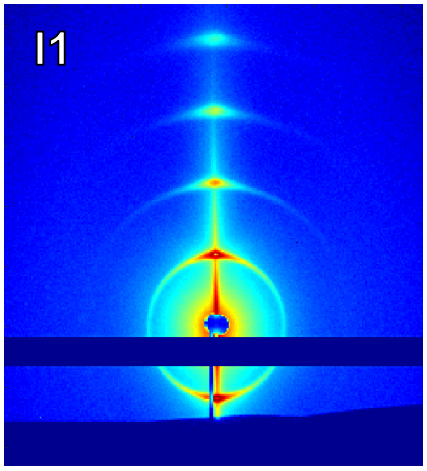
N_{bb} = 339, d^* = 46.2 nm



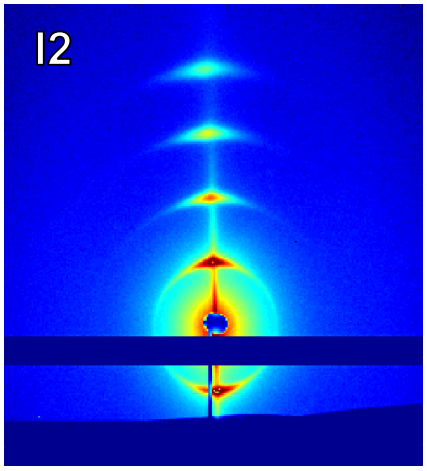
Note: **H** samples exhibit minor HEX character (*i.e.*, weak isotropic $\sqrt{7}$ peak). The presence of minor HEX is not expected to affect d^*.

System I, z = 0

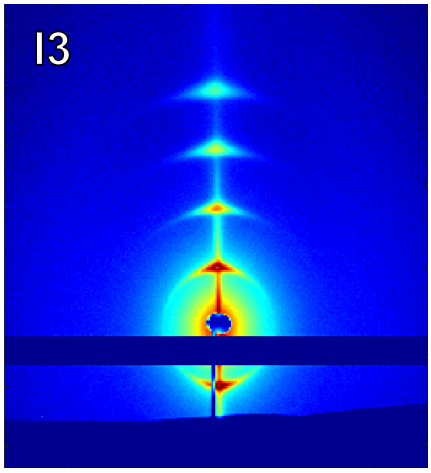
N_{bb} = 184, d^* = 26.3 nm



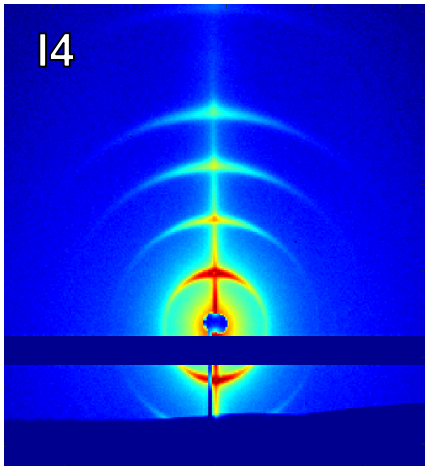
N_{bb} = 219, d^* = 29.5 nm



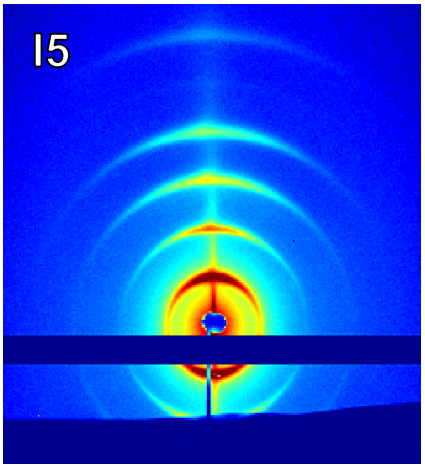
N_{bb} = 249, d^* = 32.1 nm



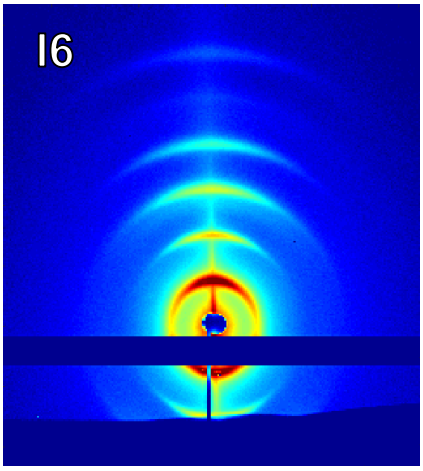
N_{bb} = 287, d^* = 35.4 nm



N_{bb} = 326, d^* = 38.9 nm

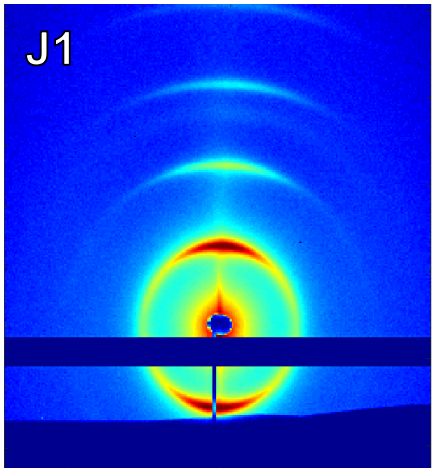


N_{bb} = 363, d^* = 41.6 nm

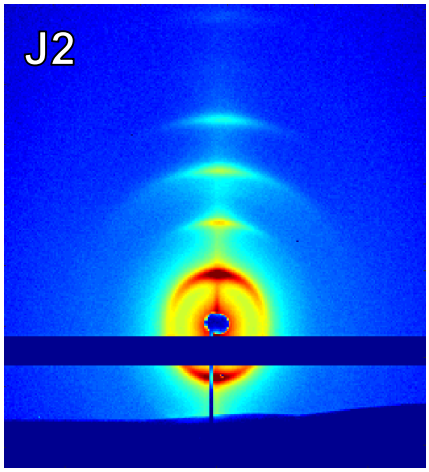


System II, z = 0.75

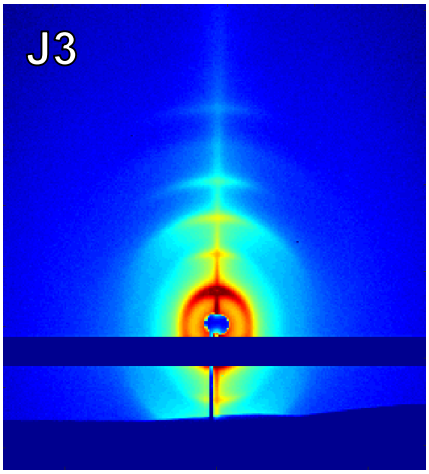
N_{bb} = 44, d^* = 2 3.5 nm



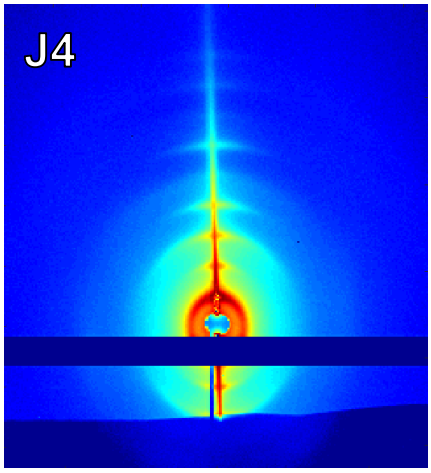
N_{bb} = 82, d^* = 36.8 nm



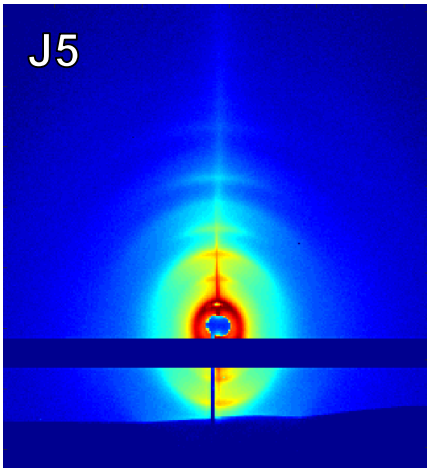
N_{bb} = 125, d^* = 52.4 nm



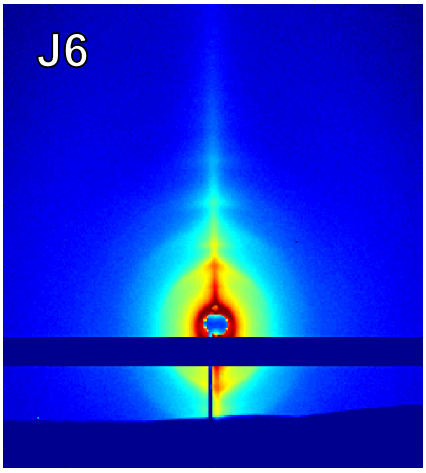
N_{bb} = 152, d^* = 62.6 nm



N_{bb} = 198, d^* = 76.0 nm

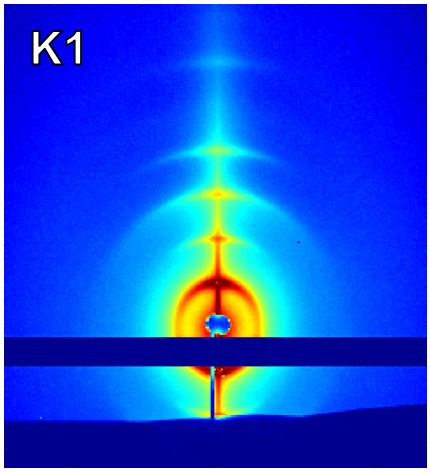


N_{bb} = 246, d^* = 92.0 nm

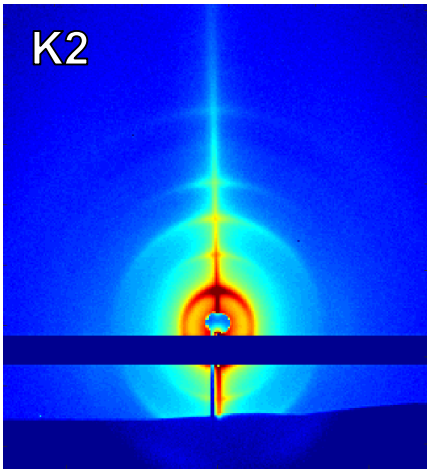


System II, $z = 0.50$

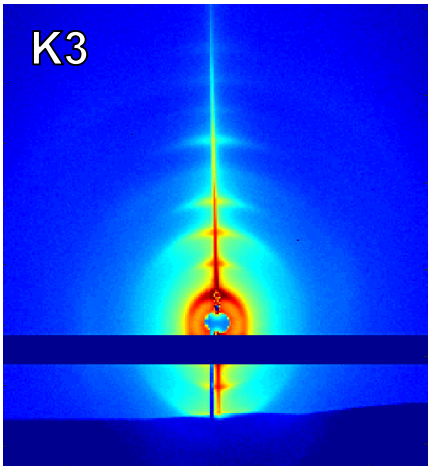
N_{bb} = 135, d^* = 43.0 nm



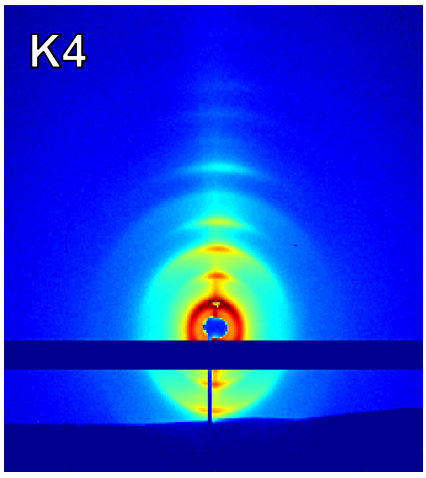
N_{bb} = 174, d^* = 52.8 nm



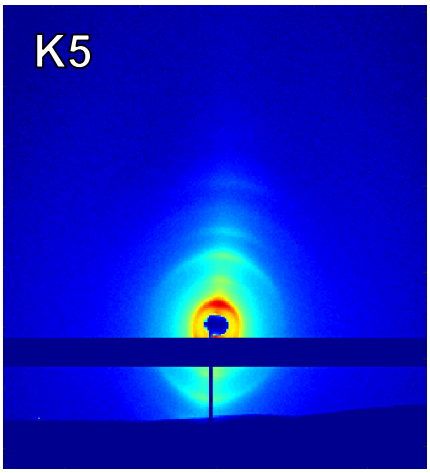
N_{bb} = 213, d^* = 62.2 nm



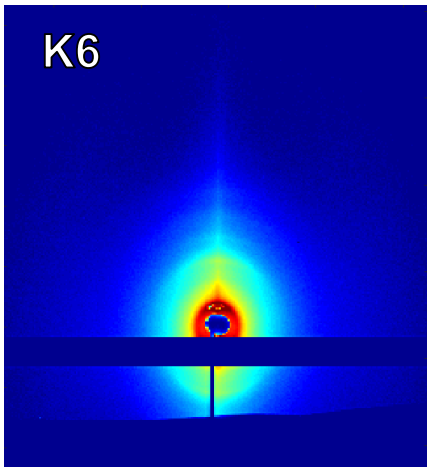
N_{bb} = 254, d^* = 70.2 nm



N_{bb} = 285, d^* = 78.0 nm

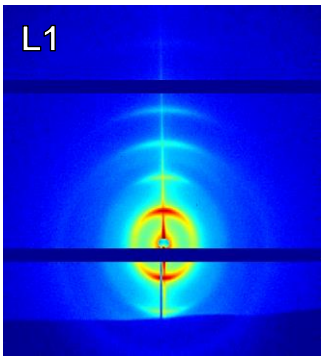


N_{bb} = 325, d^* = 85.7 nm

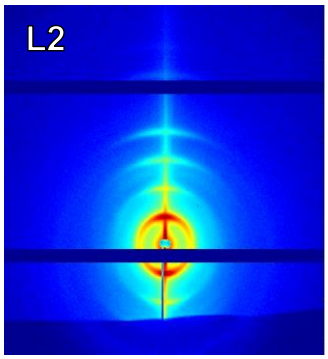


System II, z = 0.35

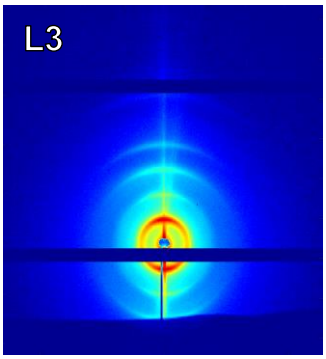
N_{bb} = 174, d^* = 46.5 nm



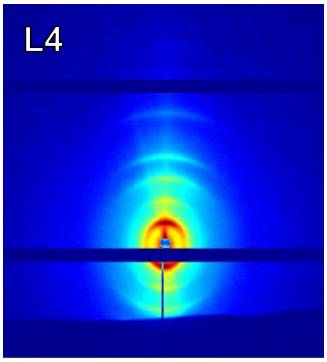
N_{bb} = 221, d^* = 55.0 nm



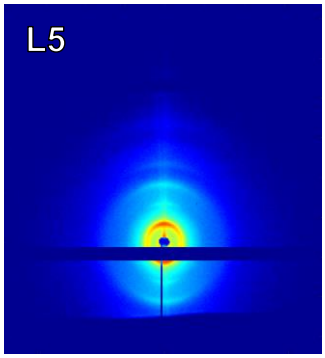
N_{bb} = 263, d^* = 62.5 nm



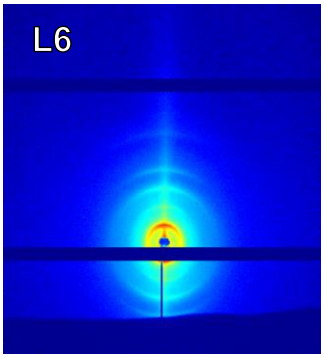
N_{bb} = 314, d^* = 71.0 nm



N_{bb} = 341, d^* = 78.0 nm



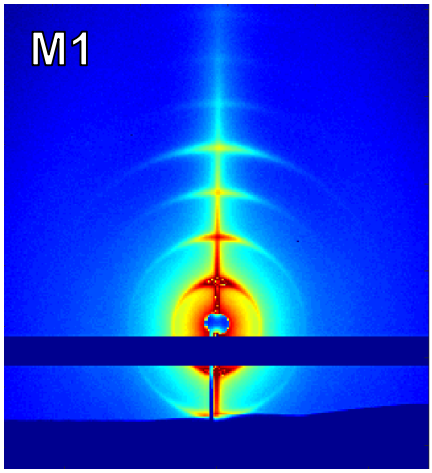
N_{bb} = 388, d^* = 85.0 nm



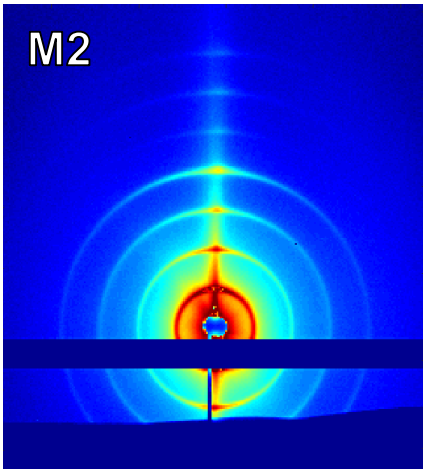
Note: **L1–L2** exhibit minor HEX character (*i.e.,* weak √7 peak). The presence of minor HEX is not expected to affect d^*.

System II, z = 0.25

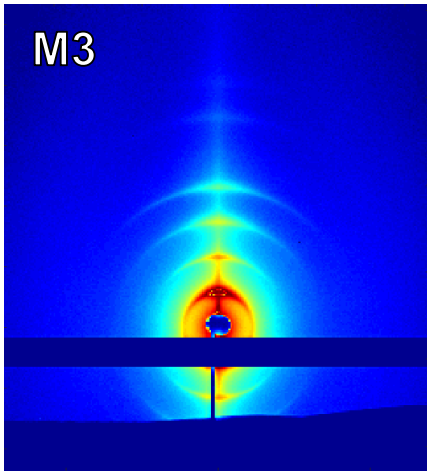
N_{bb} = 216, d^* = 42.6 nm



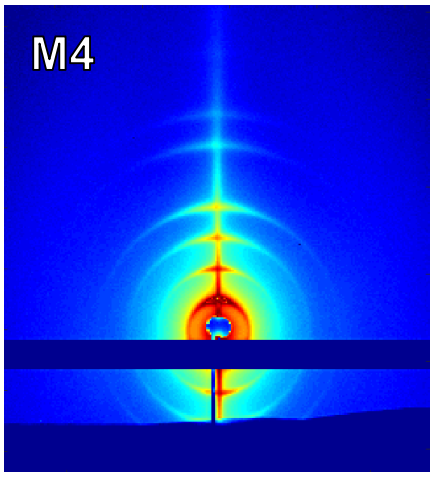
N_{bb} = 258, d^* = 48.2 nm



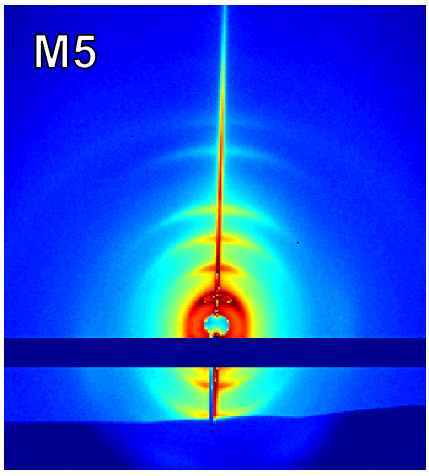
N_{bb} = 312, d^* = 54.1 nm



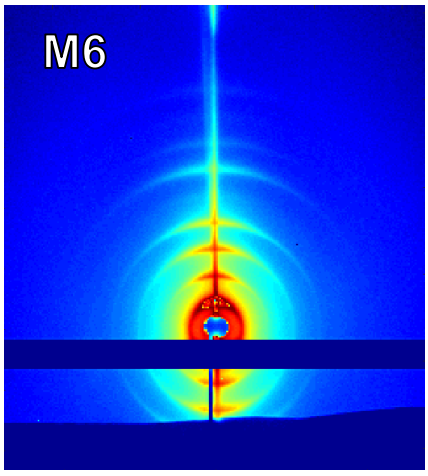
N_{bb} = 358, d^* = 61.9 nm



N_{bb} = 378, d^* = 64.0 nm

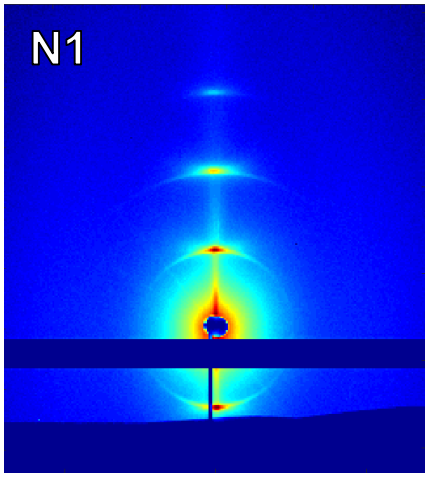


N_{bb} = 439, d^* = 71.4 nm

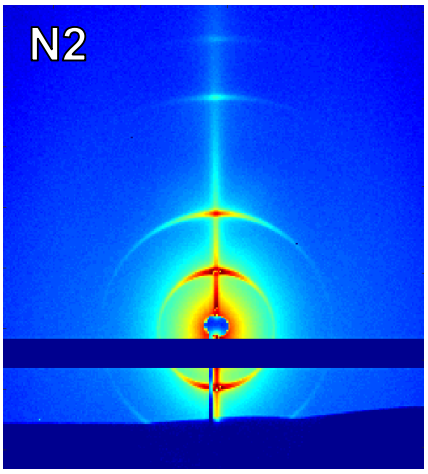


System II, z = 0.15

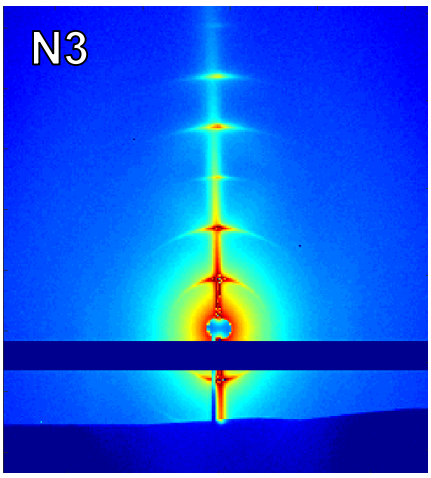
N_{bb} = 129, d^* = 24.0 nm



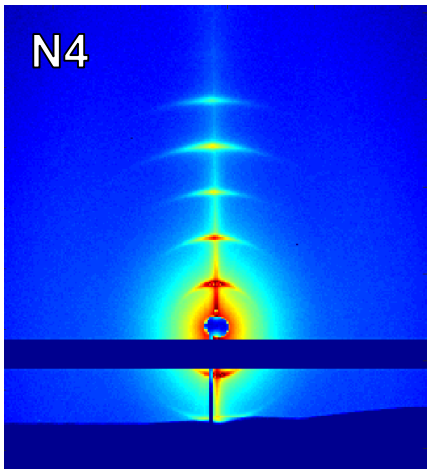
N_{bb} = 212, d^* = 32.8 nm



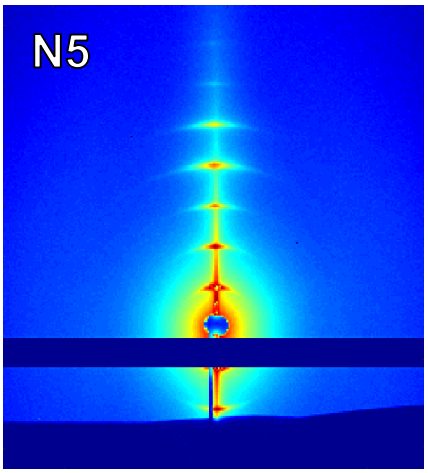
N_{bb} = 253, d^* = 37.5 nm



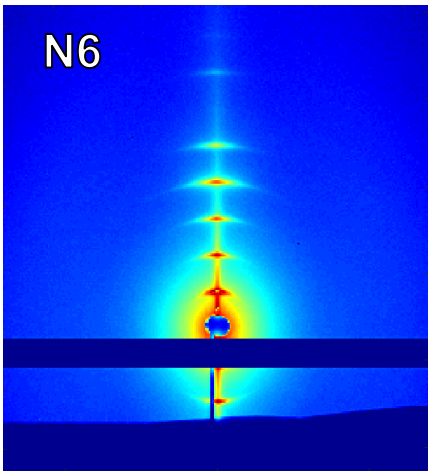
N_{bb} = 279, d^* = 41.5 nm



N_{bb} = 329, d^* = 46.6 nm

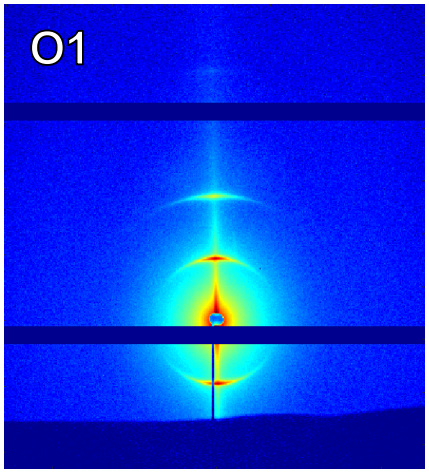


N_{bb} = 392, d^* = 51.8 nm

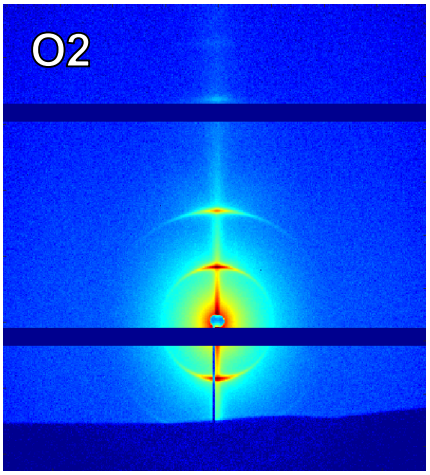


System II, $z = 0.12$

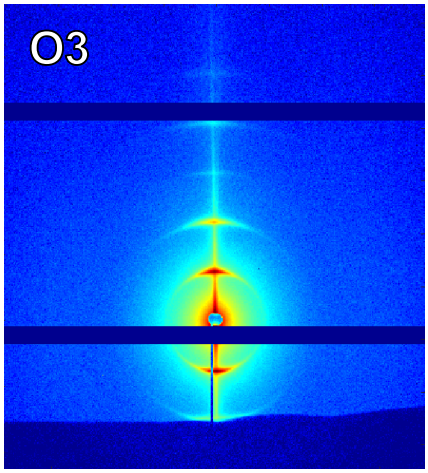
$N_{bb} = 224$, $d^* = 32.8$ nm



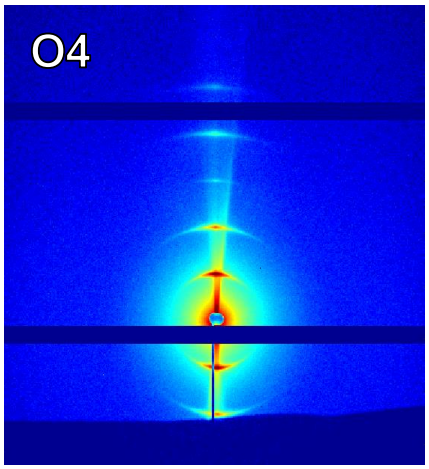
$N_{bb} = 274$, $d^* = 36.5$ nm



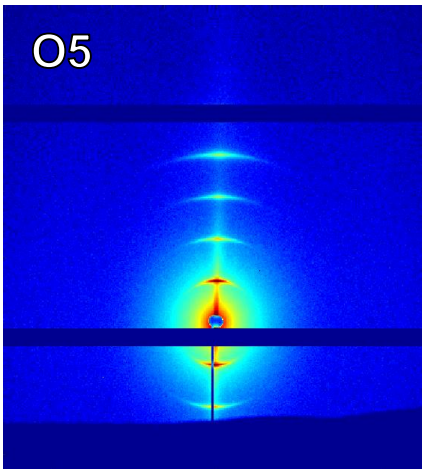
$N_{bb} = 330$, $d^* = 42.0$ nm



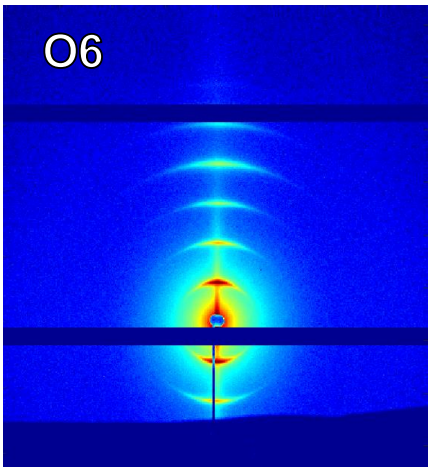
$N_{bb} = 370$, $d^* = 44.3$ nm



$N_{bb} = 409$, $d^* = 49.0$ nm

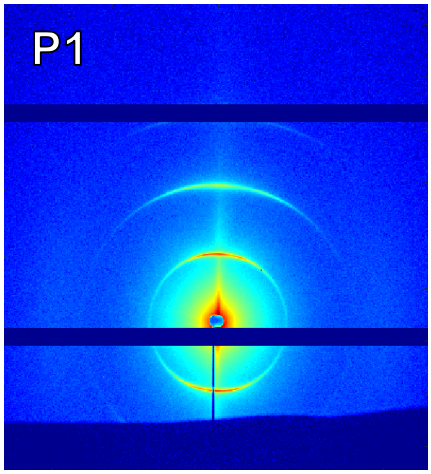


$N_{bb} = 451$, $d^* = 52.5$ nm

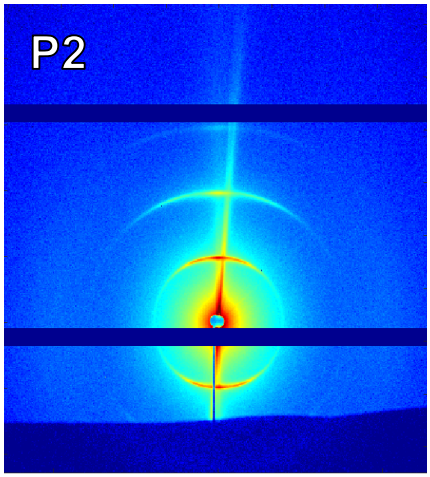


System II, z = 0.06

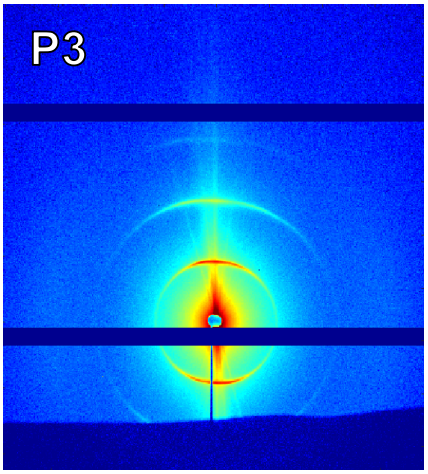
N_{bb} = 324, d^* = 30.3 nm



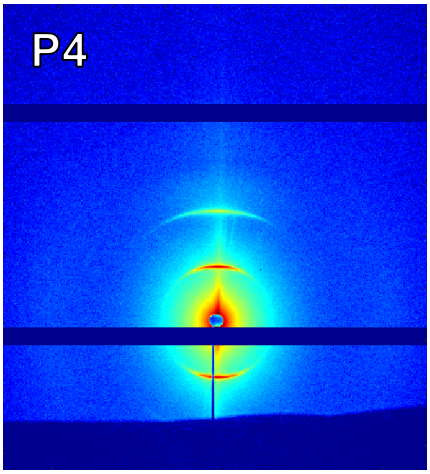
N_{bb} = 367, d^* = 31.8 nm



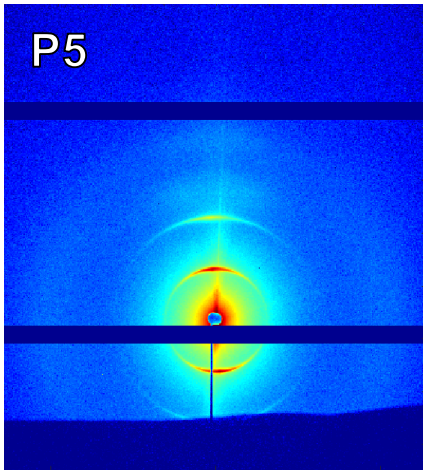
N_{bb} = 413, d^* = 34.2 nm



N_{bb} = 469, d^* = 37.3 nm

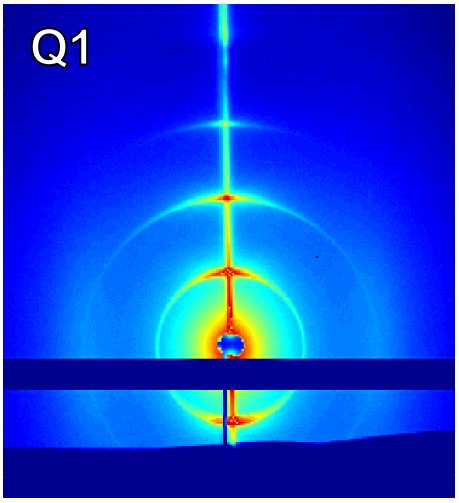


N_{bb} = 533, d^* = 40.4 nm

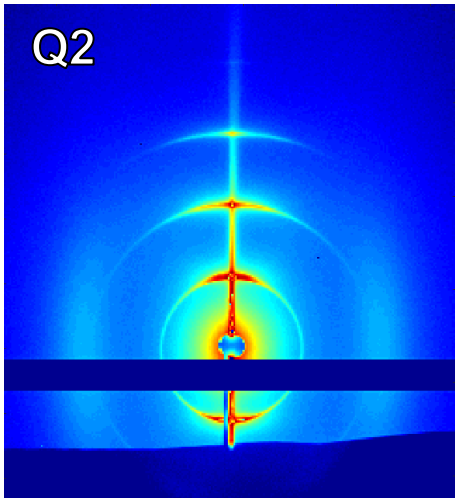


System II, $z = 0.05$

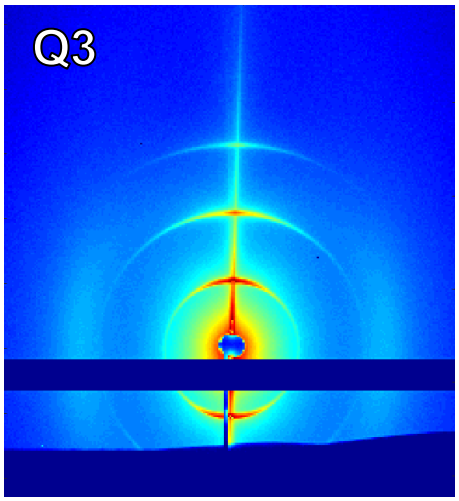
$N_{bb} = 337,\ d^* = 27.2$ nm



$N_{bb} = 376,\ d^* = 28.5$ nm



$N_{bb} = 408,\ d^* = 30.0$ nm



$N_{bb} = 451,\ d^* = 31.5$ nm